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(54) Title: FABRIC WRINKLE CONTROL COMPOSITION AND METHOD			
(57) Abstract			
<p>The present invention relates to a stable, aqueous wrinkle controlling and, optionally, odor-absorbing, composition, preferably for use on fabric. The composition comprises fabric lubricant, shape retention polymer, lithium salts, and/or plasticizers for wrinkle control and, optionally, from about 0.1 % to about 20 %, by weight of the composition, of solubilized, water-soluble, uncomplexed cyclodextrin. Optionally, the composition can contain low molecular weight polyols; metallic salts to help control odor; nonionic surfactants to improve performance and formulatability, a humectant, etc. The composition is essentially free of any material that would soil or stain fabric. The composition is preferably applied as small particle size droplets, especially from spray containers.</p>			

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FABRIC WRINKLE CONTROL COMPOSITION AND METHOD

TECHNICAL FIELD

The present invention relates to fabric care compositions and methods for treating fabrics in order to improve various properties of fabrics, in particular, reduction or removal of unwanted wrinkles.

BACKGROUND OF THE INVENTION

Wrinkles in textile fabrics are caused by the bending and creasing of the textile material which places an external portion of a filament in a yarn under tension while the internal portion of that filament in the yarn is placed under compression. Particularly with cotton fabrics, the hydrogen bonding that occurs between the cellulose molecules contributes to keeping wrinkles in place. The wrinkling of fabric, in particular clothing, is therefore subject to the inherent tensional elastic deformation and recovery properties of the fibers which constitute the yarn and fabrics.

In the modern world, with the increase of hustle and bustle and travel, there is a demand for a quick fix which will help to diminish the labor involved in home laundering and/or the cost and time involved in dry cleaning or commercial laundering. This has brought additional pressure to bear on textile technologists to produce a product that will sufficiently reduce wrinkles in fabrics, especially clothing, and to produce a good appearance through a simple, convenient application of a product.

U.S. Pat. No. 5,532,023, issued Jul. 2, 1996 to Vogel, Wahl, Cappel and Ward discloses aqueous wrinkle control composition containing non-volatile silicone and film forming polymer. Preferred silicones include reactive silicones and amino-functional silicone, known as "amodimethicone". The composition containing such silicones is applied to fabric from a spray dispenser. It is found that in the spray treatment, an amount of the aqueous composition misses the fabric, but instead falls on flooring surfaces, such as rugs, carpets, concrete floors, tiled floors, linoleum floors, bathtub floors, and leave a silicone layer that is accumulated and/or cured and/or bonded to the flooring surfaces. Such silicones that are accumulated on such surfaces, and especially those that are bonded to such surfaces are difficult to remove. Flooring surfaces thus become slippery and can present a safety hazard to the household members. U.S. Pat. No. 5,573,695, issued Nov. 12, 1996 to E. F. Targosz discloses an aqueous wrinkle removal composition containing a vegetable oil based cationic quaternary ammonium surfactant, and an anionic fluorosurfactant. Similarly, U.S. Pat. No. 4,661,268, issued Apr. 28, 1987 to Jacobson et al. discloses a wrinkle removal spray comprising an aqueous alcoholic composition containing a dialkyl quaternary ammonium salt and a

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silicone surfactant and/or a fluoro surfactant. U.S. Pat. No. 5,100,566, issued Mar. 31, 1992 to Agbomeirele et al., discloses a method of reducing wrinkles in fabric by spraying the fabric with an aqueous alcoholic solution of an anionic siliconate alkali metal salt. U.S. Pat. No. 4,806,254, issued Feb. 21, 1989 to J. A. Church discloses fabric wrinkle removal aqueous alcoholic solution containing glycerine and a nonionic surfactant. These patents are incorporated herein by reference.

The present invention reduces wrinkles in fabrics, including clothing, dry cleanables, and draperies, without the need for ironing. The present invention can be used on damp or dry clothing to relax wrinkles and give clothes a ready to wear look that is demanded by today's fast paced world. The present invention also essentially eliminates the need for touch up ironing usually associated with closet, drawer, and suitcase storage of garments.

In a preferred aspect, an additional benefit of the composition of the present invention is an improved garment shape, body and crispness.

When ironing is desired however, the composition of the present invention can also act as an excellent ironing aid. The present invention makes the task of ironing easier and faster by creating less iron drag. When used as an ironing aid, the composition of the present invention help produce a crisp, smooth appearance.

SUMMARY OF THE INVENTION

The present invention relates to a stable, preferably translucent, more preferably clear, aqueous fabric wrinkle controlling composition, fabric wrinkle control methods, and articles of manufacture that use such fabric wrinkle controlling composition. The fabric wrinkle control composition comprises:

- (A). an effective amount of a wrinkle control agent, selected from the group consisting of fabric lubricant, shape retention polymer, lithium salts, and mixtures thereof, preferably from about 0.05% to about 5%, more preferably from about 0.2% to about 3%, even more preferably from about 0.3% to about 2% by weight of the usage composition;
- (B). optionally, an effective amount to soften fibers and/or soften shape retention polymer, when present, of hydrophilic plasticizer wrinkle control agent;
- (C). optionally, but preferably, to reduce surface tension, and/or to improve performance and formulatability, an effective amount of surfactant;
- (D). optionally, but preferably, an effective amount to absorb malodor, of an odor control agent;

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- (E). optionally, but preferably, an effective amount to provide olfactory effects of perfume;
- (F). optionally, an effective amount, to kill, or reduce the growth of microbes, of antimicrobial active;
- (G). optionally, an effective amount to provide improved antimicrobial action of aminocarboxylate chelator;
- (H). optionally, an effective amount of solubilized, water-soluble, antimicrobial preservative; and
- (I). aqueous carrier,

said composition preferably being essentially free of any material that would soil or stain fabric under usage conditions and said composition preferably either having volatile silicone as the fabric lubricant, shape retention polymer that contains an effective amount of carboxyl groups to control amine odor, or lithium salts and/or said composition being applied as small droplets to the fabric.

The present invention also relates to concentrated compositions, which are diluted to form compositions with the usage concentrations, as given hereinabove, for use in the "usage conditions".

The present invention also relates to the compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of articles and/or surfaces with said compositions containing wrinkle control agent and other optional ingredients at a level that is effective, yet is not discernible when dried on the surfaces. The spray dispenser comprises manually activated and non-manual powered (operated) spray means and a container containing the wrinkle controlling composition.

The present invention also comprises the use of small particle diameter droplets of the compositions herein to treat fabrics, to provide superior performance, e.g., the method of applying the compositions to fabrics, etc. as very small particles (droplets) preferably having weight average diameter particle sizes (diameters) of from about 5 μm to about 250 μm , more preferably from about 10 μm to about 120 μm , and even more preferably from about 20 μm to about 100 μm .

DETAILED DESCRIPTION OF THE INVENTION

As discussed before, the present invention relates to methods and compositions for fabric wrinkle control that utilize, at least in an effective amount, preferably from about 0.05% to about 5%, more preferably from about 0.2% to about 3%, and even more preferably from about 0.3% to about 2% by weight of the usage composition, of wrinkle control agent, selected from the group consisting of fabric (fiber) lubricant, shape retention polymer, lithium salts, and mixtures thereof.

Fiber lubricants impart a lubricating property or increased gliding ability to fibers in fabric, particularly clothing. Not to be bound by theory, it is believed that water and other alcoholic solvents break or weaken the hydrogen bonds that hold the wrinkles, the fabric lubricant facilitates the ability of the fibers to glide on one another to further release the fibers from the wrinkle condition in wet or damp fabric. After the fabric is dried, the residual silicone can provide lubricity to reduce the tendency of fabric rewrinkling.

Specifically, the preferred fabric lubricant is dimethylsiloxane silicone, more preferably volatile dimethylsiloxane. The volatile silicones provide surprisingly good fiber lubrication without the risk of unacceptable build-up on the fabric and/or surrounding surfaces due to their volatile nature. The volatile silicones also provide a desirable control over the formation of wrinkles in fabrics while the fabrics are being dried. When silicone is present, it is present at least at an effective amount to provide lubrication of the fibers, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3%, more preferably from about 0.3% to about 2%, by weight of the usage composition.

The shape retention polymers can be natural, or synthetic, and can act by forming a film, and/or by providing adhesive properties. E.g., the present invention can optionally use film-forming and/or adhesive polymer to impart shape retention to fabric, particularly clothing. The preferred shape retention polymer is copolymer containing hydrophilic unsaturated organic mono-carboxylic and polycarboxylic acid monomers, and salts thereof, and mixtures thereof, more preferably copolymer containing hydrophobic monomers and hydrophilic monomers wherein the hydrophilic monomers include unsaturated organic mono-carboxylic and polycarboxylic acid monomers, and salts thereof, and mixtures thereof. The preferred shape retention polymers of the current invention surprisingly provide control of certain amine type malodors on fabrics, in addition to providing the fabric wrinkle control benefit. When the shape retention polymer is present, it is present at least at an effective amount to provide wrinkle control and/or shape retention, typically from about 0.05% to about 10%, preferably from about 0.1% to about 5%, more preferably from about 0.2% to about 3%, even more preferably from about 0.3% to about 1.5%, by weight of the usage composition.

Aqueous compositions comprising lithium salts and/or lithium salt hydrates provide improved fabric wrinkle control. The preferred lithium salt is lithium bromide, lithium lactate, and/or mixtures thereof. Useful levels of lithium salts are from about 0.1% to about 10%, preferably from about 0.5% to about 7%, and more preferably from about 1% to about 5%, by weight of the usage composition.

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In highly preferred versions, the compositions can also comprise:

- (B). optionally, an effective amount of hydrophilic plasticizer, e.g., from about 0.01% to about 5%, preferably from about 0.05% to about 2%, more preferably from about 0.1% to about 1% by weight of the usage composition, for improved wrinkle control and fabric feel;
- (C). optionally, but preferably, to reduce surface tension and/or to improve performance and formulatability, an effective amount of surfactant, e.g., from about 0.01% to about 5%, preferably from about 0.05% to about 3%, and more preferably from about 0.1% to about 2%, and even more preferably from about 0.2% to about 1%, by weight of the usage composition; a preferred surfactant for use to dissolve shape retention polymers is an alkyl ethoxylate surfactant having a C₈-C₁₆ alkyl group and containing from about 2 to about 6 ethyleneoxy groups, more preferably having a C₈-C₁₅ alkyl group and contains from about 2 to about 4 ethyleneoxy groups;
- (D). optionally, but preferably, an effective amount to reduce malodor, of an odor control agent, selected from the group consisting of uncomplexed cyclodextrin (preferably β -cyclodextrin, α -cyclodextrin, γ -cyclodextrin, water-soluble derivatives thereof, and mixtures thereof); metal salt (preferably zinc salt, copper salt, and mixtures thereof); water-soluble alkali metal carbonate and/or bicarbonate salts (preferably sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, and mixtures thereof); enzyme (preferably proteases); zeolites; activated carbon; low molecular weight polyacrylic acid; and mixtures thereof;
- (E). optionally, but preferably, an effective amount to provide olfactory effects of perfume, typically from about 0.003% to about 0.5%, preferably from about 0.01% to about 0.3%, more preferably from about 0.05% to about 0.2%, by weight of the usage composition;
- (F). optionally, an effective amount, to kill, or reduce the growth of microbes, of antimicrobial active; preferably from about 0.001% to about 2%, more preferably from about 0.002% to about 1%, even more preferably from about 0.003% to about 0.3%, by weight of the usage composition;
- (G). optionally, an effective amount to assist in antimicrobial action of aminocarboxylate chelator; preferably from about 0.001% to about 0.3%,

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preferably from about 0.01% to about 0.1%, more preferably from about 0.02% to about 0.05%, by weight of the usage composition;

(H). optionally, an effective amount of solubilized, water-soluble, antimicrobial preservative; and

(I). aqueous carrier,

said composition being preferably translucent, and more preferably clear, and preferably being essentially free of any material that would soil or stain fabric under usage conditions.

The present invention also relates to fabric wrinkle control methods and articles of manufacture that use such fabric wrinkle control composition. Thus the present invention relates to the compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of fabric surfaces with said fabric wrinkle control compositions containing a wrinkle control agent and other optional ingredients at a level that is effective, yet is not discernible when dried on the surfaces. The spray dispenser comprises manually activated and non-manual powered spray means and a container containing the odor-absorbing composition.

The present invention also relates to concentrated compositions, wherein the level of wrinkle control agent is from about 1% to about 20%, preferably from about 2% to about 15%, more preferably from about 3% to about 10%, by weight of the concentrated composition. The concentrated composition is typically diluted to form usage compositions, with the usage concentration of, e.g., from about 0.05% to about 5%, by weight of the usage composition, of wrinkle control active as given hereinabove. Specific levels of other optional ingredients in the concentrated composition can readily be determined from the desired usage composition and the desired degree of concentration.

I. COMPOSITION

WRINKLE CONTROL AGENT

The composition contains an effective amount of a fabric wrinkle control agent, preferably selected from the group consisting of: fiber lubricant, shape retention polymer, lithium salt, optional hydrophilic plasticizer, and mixtures thereof.

(1) Fiber Lubricants

The present invention can use fiber lubricants to impart a lubricating property, or increased gliding ability, to fibers in fabric, particularly clothing. Not to be bound by theory, it is believed that water and other alcoholic solvents break, or weaken, the hydrogen bonds that hold the wrinkles in fabric, and fabric lubricants facilitate the

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movement of fibers with respect to one another (glide) to further release the fibers from the wrinkle condition in wet or damp fabrics. After the fabric is dried, the residual fiber lubricant, especially silicone, can provide lubricity to reduce the tendency of fabric to rewrinkle.

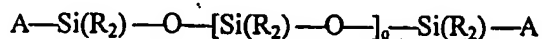
(a) Silicone

The present invention can use silicone, a preferred fiber lubricant, to impart a lubricating property, or increased gliding ability, to fibers in fabric, particularly clothing. Nonlimiting examples of useful silicones in the composition of the present invention include noncurable silicones such as polydimethylsilicone and volatile silicones, and curable silicones such as aminosilicones, phenylsilicones and hydroxysilicones. The word "silicone" as used herein preferably refers to emulsified silicones, including those that are commercially available and those that are emulsified in the composition, unless otherwise described. Preferably, the silicones are hydrophobic; are neither irritating, toxic, nor otherwise harmful when applied to fabric or when they come in contact with human skin; are chemically stable under normal use and storage conditions; and are capable of being deposited on fabric.

When the composition of this invention is to be dispensed from a spray dispenser in a consumer household setting, the noncurable silicones such as polydimethylsilicone, especially the volatile silicones, are preferred. Curable and/or reactive silicones such as amino-functional silicones and silicones with reactive groups such as Si-OH, Si-H, silanes, and the like, are not preferred in this situation, because the portion of the composition that is sprayed but misses the garment, and falls instead on flooring surfaces, such as rug, carpet, concrete floor, tiled floor, linoleum floor, bathtub floor, can leave a silicone layer that is cured and/or bonded to the flooring surfaces. Such silicones that are bonded to surfaces are difficult to be removed from the flooring surfaces. Flooring surfaces thus become slippery and can present a safety hazard to the household members. The curable and reactive silicones can be used in compositions specifically designed for use in enclosed areas such as in a dewrinkling cabinet. Many types of aminofunctional silicones also cause fabric yellowing. Thus, the silicones that cause fabric discoloration are also not preferred.

The preferred silicone is volatile silicone fluid which can be a cyclic silicone fluid of the formula $[(CH_3)_2SiO]_n$ where n ranges between about 3 to about 7, preferably about 5, or a linear silicone polymer fluid having the formula $(CH_3)_3SiO[(CH_3)_2SiO]_mSi(CH_3)_3$ where m can be 0 or greater and has an average value such that the viscosity at 25°C of the silicone fluid is preferably about 5 centistokes or less.

The non-volatile silicones that are useful in the composition of the present invention is polyalkyl and/or phenylsilicones silicone fluids and gums with the following structure:



The alkyl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicones remain fluid at room temperature.

Each R group preferably can be alkyl, aryl, hydroxy, or hydroxyalkyl group, and mixtures thereof, more preferably, each R is methyl, ethyl, propyl or phenyl group, most preferably R is methyl. Each A group which blocks the ends of the silicone chain can be hydrogen, methyl, methoxy, ethoxy, hydroxy, propoxy, and aryloxy group, preferably methyl. Suitable A groups include hydrogen, methyl, methoxy, ethoxy, hydroxy, and propoxy. q is preferably an integer from about 7 to about 8,000. The preferred silicones are polydimethyl siloxanes; more preferred silicones are polydimethyl siloxanes having a viscosity of from about 50 to about 1000,000 centistokes at 25°C. Mixtures of volatile silicones and non-volatile polydimethyl siloxanes are also preferred. Suitable examples include silicones offered by Dow Corning Corporation and General Electric Company.

Other useful silicone materials, but less preferred than polydimethyl siloxanes, include materials of the formula:

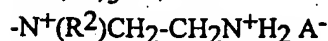
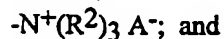
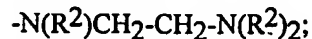


wherein x and y are integers which depend on the molecular weight of the silicone, preferably having a viscosity of from about 10,000 cst to about 500,000 cst at 25°C. This material is also known as "amodimethicone". Although silicones with a high number, e.g., greater than about 0.5 millimolar equivalent of amine groups can be used, they are not preferred because they can cause fabric yellowing.

Similarly, silicone materials which can be used correspond to the formulas:



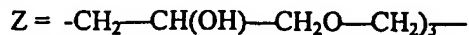
wherein G is selected from the group consisting of hydrogen, phenyl, OH, and/or C₁-C₈ alkyl; a denotes 0 or an integer from 1 to 3; b denotes 0 or 1; the sum of n + m is a number from 1 to about 2,000; R¹ is a monovalent radical of formula C_pH_{2p}L in which p is an integer from 2 to 8 and L is selected from the group consisting of:



wherein each R^2 is chosen from the group consisting of hydrogen, phenyl, benzyl, saturated hydrocarbon radical, and each A^- denotes compatible anion, e.g., a halide ion; and



wherein



R^3 denotes a long chain alkyl group; and

f denotes an integer of at least about 2.

In the formulas herein, each definition is applied individually and averages are included.

Another silicone material which can be used, but is less preferred than polydimethyl siloxanes, has the formula:



wherein n and m are the same as before. The preferred silicones of this type are those which do not cause fabric discoloration.

Alternatively, the silicone material can be provided as a moiety or a part of a non-silicone molecule. Examples of such materials are copolymers containing silicone moieties, typically present as block and/or graft copolymers.

When silicone is present, it is present at least an effective amount to provide lubrication of the fibers, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3%, more preferably from about 0.3% to about 2%, by weight of the usage composition.

When optional cyclodextrin is present in the composition, the silicone needs to be compatible with the cyclodextrin, that is, it should not substantially form complex with cyclodextrin so as to diminish performance of the cyclodextrin and/or the silicone. Complex formation diminishes both the ability of the cyclodextrin to absorb odors and the ability of the silicone to provide fiber lubricity. In general, the preferred cyclodextrin compatible silicones have pendant alkyl groups having less than about 8, preferably less than about 6, carbon atoms, and do not have pendant aryl, e.g., phenyl or benzyl groups.

(b) Synthetic solid particles

Solid polymeric particles of average particle size smaller than about 10 microns, preferably smaller than 5 microns, more preferably smaller than about 1 micron, e.g., Velustrol P-40 oxidized polyethylene emulsion available from Clariant, can be used as a

lubricant, since they can provide a "roller-bearing" action. When solid polymeric particles are present, they are present at an effective amount to provide lubrication of the fibers, typically from about 0.01% to about 3%, preferably from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of the usage composition.

(2) Shape Retention Polymer

These polymers can be natural, or synthetic, and can act by forming a film, and/or by providing adhesive properties. E.g., the present invention can optionally use film-forming and/or adhesive polymer to impart shape retention to fabric, particularly clothing. By "adhesive" it is meant that when applied as a solution or a dispersion to a fiber surface and dried, the polymer can attach to the surface. The polymer can form a film on the surface, or when residing between two fibers and in contact with the two fibers, it can bond the two fibers together. Other polymers such as starches can form a film and/or bond the fibers together when the treated fabric is pressed by a hot iron. Such a film will have adhesive strength, cohesive breaking strength, and cohesive breaking strain.

Nonlimiting examples for natural polymers are starches and their derivatives, and chitins and their derivatives.

The synthetic polymers useful in the present invention are comprised of monomers. Some nonlimiting examples of monomers which can be used to form the synthetic polymers of the present invention include: low molecular weight C_1 - C_6 unsaturated organic mono-carboxylic and polycarboxylic acids, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and mixtures thereof; esters of said acids with C_1 - C_{12} alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, neodecanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, and the like, and mixtures thereof. Nonlimiting examples of said esters are methyl acrylate, ethyl acrylate, t-butyl acrylate, methyl methacrylate, hydroxyethyl methacrylate, methoxy ethyl methacrylate, and mixtures thereof; amides and imides of said acids, such as N,N-dimethylacrylamide, N-t-butyl acrylamide, maleimides; low molecular weight unsaturated alcohols such as vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization), allyl alcohol; esters of said alcohols with low molecular weight carboxylic acids, such as, vinyl acetate, vinyl propionate; ethers of said alcohols such as

methyl vinyl ether; aromatic vinyl such as styrene, alpha-methylstyrene, t-butylstyrene, vinyl toluene, polystyrene macromer, and the like; polar vinyl heterocyclics, such as vinyl pyrrolidone, vinyl caprolactam, vinyl pyridine, vinyl imidazole, and mixtures thereof; other unsaturated amines and amides, such as vinyl amine, diethylene triamine, dimethylaminoethyl methacrylate, ethenyl formamide; vinyl sulfonate; salts of acids and amines listed above; low molecular weight unsaturated hydrocarbons and derivatives such as ethylene, propylene, butadiene, cyclohexadiene, vinyl chloride; vinylidene chloride; and mixtures thereof and alkyl quaternized derivatives thereof, and mixtures thereof. Preferably, said monomers are selected from the group consisting of vinyl alcohol; acrylic acid; methacrylic acid; methyl acrylate; ethyl acrylate; methyl methacrylate; t-butyl acrylate; t-butyl methacrylate; n-butyl acrylate; n-butyl methacrylate; isobutyl methacrylate; 2-ethylhexyl methacrylate; dimethylaminoethyl methacrylate; N,N-dimethyl acrylamide; N,N-dimethyl methacrylamide; N-t-butyl acrylamide; vinylpyrrolidone; vinyl pyridine; adipic acid; diethylenetriamine; salts thereof and alkyl quaternized derivatives thereof, and mixtures thereof.

Preferably, said monomers form homopolymers and/or copolymers (i.e., the film-forming and/or adhesive polymer) having a glass transition temperature (T_g) of from about -20°C to about 150°C , preferably from about -10°C to about 150°C , more preferably from about 0°C to about 100°C , most preferably, the adhesive polymer hereof, when dried to form a film will have a T_g of at least about 25°C ., so that they are not unduly sticky, or "tacky" to the touch. Preferably said polymer is soluble and/or dispersible in water and/or alcohol. Said polymer typically has a molecular weight of at least about 500, preferably from about 1,000 to about 2,000,000, more preferably from about 5,000 to about 1,000,000, and even more preferably from about 30,000 to about 300,000 for some polymers.

Some non-limiting examples of homopolymers and copolymers which can be used as film-forming and/or adhesive polymers of the present invention are: adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer; adipic acid/epoxypropyl diethylenetriamine copolymer; poly(vinylpyrrolidone/dimethylaminoethyl methacrylate); polyvinyl alcohol; polyvinylpyridine n-oxide; methacryloyl ethyl betaine/methacrylates copolymer; ethyl acrylate/methyl methacrylate/methacrylic acid/acrylic acid copolymer; polyamine resins; and polyquaternary amine resins; poly(ethenylformamide); poly(vinylamine) hydrochloride; poly(vinyl alcohol-co-6% vinylamine); poly(vinyl alcohol-co-12% vinylamine); poly(vinyl alcohol-co-6% vinylamine hydrochloride); and poly(vinyl alcohol-co-12% vinylamine hydrochloride). Preferably, said copolymer and/or homopolymers are

selected from the group consisting of adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer; poly(vinylpyrrolidone/dimethylaminoethyl methacrylate); polyvinyl alcohol; ethyl acrylate/methyl methacrylate/methacrylic acid/acrylic acid copolymer; methacryloyl ethyl betaine/methacrylates copolymer; polyquaternary amine resins; poly(ethenylformamide); poly(vinylamine) hydrochloride; poly(vinyl alcohol-co-6% vinylamine); poly(vinyl alcohol-co-12% vinylamine); poly(vinyl alcohol-co-6% vinylamine hydrochloride); and poly(vinyl alcohol-co-12% vinylamine hydrochloride).

Nonlimiting examples of the preferred polymer that are commercially available are: polyvinylpyrrolidone/dimethylaminoethyl methacrylate copolymer, such as Copolymer 958[®], molecular weight of about 100,000 and Copolymer 937, molecular weight of about 1,000,000, available from GAF Chemicals Corporation; adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer, such as Cartaretin F-4[®] and F-23, available from Sandoz Chemicals Corporation; methacryloyl ethyl betaine/methacrylates copolymer, such as Diaformer Z-SM[®], available from Mitsubishi Chemicals Corporation; polyvinyl alcohol copolymer resin, such as Vinex 2019[®], available from Air Products and Chemicals or Moweol[®], available from Clariant; adipic acid/epoxypropyl diethylenetriamine copolymer, such as Delsette 101[®], available from Hercules Incorporated; polyamine resins, such as Cypro 515[®], available from Cytec Industries; polyquaternary amine resins, such as Kymene 557H[®], available from Hercules Incorporated; and polyvinylpyrrolidone/acrylic acid, such as Sokalan EG 310[®], available from BASF.

Preferred polymers useful in the present invention are selected from the group consisting of copolymers of hydrophilic monomers and hydrophobic monomers. The polymer can be linear random or block copolymers, and mixtures thereof. Such hydrophobic/hydrophilic copolymers typically have a hydrophobic monomer/hydrophilic monomer ratio of from about 95:5 to about 20:80, preferably from about 90:10 to about 40:60, more preferably from about 80:20 to about 50:50 by weight of the copolymer. The hydrophobic monomer can comprise a single hydrophobic monomer or a mixture of hydrophobic monomers, and the hydrophilic monomer can comprise a single hydrophilic monomer or a mixture of hydrophilic monomers. The term "hydrophobic" is used herein consistent with its standard meaning of lacking affinity for water, whereas "hydrophilic" is used herein consistent with its standard meaning of having affinity for water. As used herein in relation to monomer units and polymeric materials, including the copolymers, "hydrophobic" means substantially water insoluble; "hydrophilic" means substantially water soluble. In this regard, "substantially water insoluble" shall refer to a material that is not soluble in distilled (or equivalent) water, at 25°C., at a concentration of about 0.2%

by weight, and preferably not soluble at about 0.1% by weight (calculated on a water plus monomer or polymer weight basis). "Substantially water soluble" shall refer to a material that is soluble in distilled (or equivalent) water, at 25°C., at a concentration of about 0.2% by weight, and are preferably soluble at about 1% by weight. The terms "soluble", "solubility" and the like, for purposes hereof, corresponds to the maximum concentration of monomer or polymer, as applicable, that can dissolve in water or other solvents to form a homogeneous solution, as is well understood to those skilled in the art.

Nonlimiting examples of useful hydrophobic monomers are acrylic acid C₁-C₁₈ alkyl esters, such as methyl acrylate, ethyl acrylate, t-butyl acrylate; methacrylic C₁-C₁₈ alkyl esters, such as methyl methacrylate, 2-ethyl hexyl methacrylate, methoxy ethyl methacrylate; vinyl alcohol esters of carboxylic acids, such as, vinyl acetate, vinyl propionate, vinyl neodecanoate; aromatic vinyls, such as styrene, t-butyl styrene, vinyl toluene; vinyl ethers, such as methyl vinyl ether; vinyl chloride; vinylidene chloride; ethylene, propylene and other unsaturated hydrocarbons; and the like; and mixtures thereof. Some preferred hydrophobic monomers are methyl acrylate, methyl methacrylate, t-butyl acrylate, t-butyl methacrylate, n-butyl acrylate, n-butyl methacrylate, and mixtures thereof.

Nonlimiting examples of useful hydrophilic monomers are unsaturated organic mono-carboxylic and polycarboxylic acids, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid; unsaturated alcohols, such as vinyl alcohol, allyl alcohol; polar vinyl heterocyclics, such as vinyl pyrrolidone, vinyl caprolactam, vinyl pyridine, vinyl imidazole; vinyl amine; vinyl sulfonate; unsaturated amides, such as acrylamides, e.g., N,N-dimethylacrylamide, N-t-butyl acrylamide; hydroxyethyl methacrylate; dimethylaminoethyl methacrylate; salts of acids and amines listed above; and the like; and mixtures thereof. Some preferred hydrophilic monomers are acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N-t-butyl acrylamide, dimethylamino ethyl methacrylate, vinyl pyrrolidone, salts thereof and alkyl quaternized derivatives thereof, and mixtures thereof.

Non limiting examples of polymers for use in the present invention include the following, where the composition of the copolymer is given as approximate weight percentage of each monomer used in the polymerization reaction used to prepare the polymer: vinyl pyrrolidone/vinyl acetate copolymers (at ratios of up to about 30% by weight of vinyl pyrrolidone); dimethyl acrylamide/ t-butyl acrylate/ethyl hexyl methacrylate copolymer (10/45/45); vinyl pyrrolidone/vinyl acetate/butyl acrylate copolymer (10/78/12 and 10/70/20); vinyl pyrrolidone/vinyl propionate copolymer (5/95); vinyl caprolactam/vinyl acetate copolymer (5/95); acrylic acid/t-butyl acrylate

(25/75) and styling resins sold under the trade names Ultrahold CA 8[®] by Ciba Geigy (ethyl acrylate/ acrylic acid/N-t-butyl acrylamide copolymer); Resyn 28-1310[®] by National Starch and Luviset CA 66[®] by BASF (vinyl acetate/crotonic acid copolymer 90/10); Luviset CAP[®] by BASF (vinyl acetate/vinyl propionate/crotonic acid 50/40/10); Resyn 28-2930[®] by National Starch (vinyl acetate/vinyl neodecanoate/crotonic acid copolymer), Amerhold DR-25[®] by Union Carbide (ethyl acrylate/methacrylic acid/methyl methacrylate/acrylic acid copolymer), and Poligen A[®] by BASF (polyacrylate dispersion).

Preferably, the shape retention polymers contain an effective amount of monomers having carboxylic groups to control amine odor. Highly preferred shape retention copolymers contain hydrophobic monomers and hydrophilic monomers which comprise unsaturated organic mono-carboxylic and polycarboxylic acid monomers, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and salts thereof, and mixtures thereof; and optionally other hydrophilic monomers. These preferred polymers of the current invention surprisingly provide control of certain amine type malodors in fabrics, in addition to providing the fabric wrinkle control benefit. Examples of the hydrophilic unsaturated organic mono-carboxylic and polycarboxylic acid monomers are acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and mixtures thereof. Nonlimiting examples of the hydrophobic monomers are esters of the unsaturated organic mono-carboxylic and polycarboxylic acids cited hereinabove with C₁-C₁₂ alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, and mixtures thereof, preferably methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, t-butanol, and mixtures thereof. One highly preferred copolymer contains acrylic acid and t-butyl acrylate monomeric units, preferably with acrylic acid/t-butyl acrylate ratios of from about 90:10 to about 10:90, preferably from about 70:30 to about 15:85, more preferably from about 40:60 to about 20:80. Nonlimiting examples of acrylic acid/tert-butyl acrylate copolymers useful in the present invention are those typically with a molecular weight of from about 1,000 to about 2,000,000, preferably from about 5,000 to about 1,000,000, and more preferably from about 30,000 to about 300,000, and with an approximate acrylic acid/tert-butyl acrylate weight ratio of about 25:75 and an average molecular weight of from about 70,000 to about 100,000, and those with an approximate acrylic acid/tert-butyl acrylate weight ratio of about 35:65 and an average molecular weight of from about 60,000 to about 90,000.

Compositions containing these polymers also can additionally comprise perfume, antibacterial active, odor control agent, static control agent, and mixtures thereof.

The film-forming and/or adhesive polymer of the present invention is present at least an effective amount to provide shape retention, typically from about 0.05% to about 10%, preferably from about 0.1% to about 5%, more preferably from about 0.2% to about 3%, even more preferably from about 0.3% to about 1.5%, by weight of the usage composition.

The adhesive polymer is present in the composition in a sufficient amount to result in an amount of from about 0.001% to about 1%, preferably from about 0.01% to about 0.5%, more preferably from about 0.02% to about 0.4% by weight of polymer per weight of dry fabrics.

It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive and film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose.

Concentrated compositions can also be used in order to provide a less expensive product. When a concentrated product is used, i.e., when the wrinkle reducing active is from about 5% to about 50%, by weight of the concentrated composition, it is preferable to dilute the composition before treating fabric. Preferably, the wrinkle reducing active is diluted with about 50% to about 10,000%, more preferably from about 50% to about 8,000%, and even more preferably from about 50% to about 5,000%, by weight of the composition, of water.

Silicones and film-forming polymers can be combined to produce preferred wrinkle reducing actives. Typically the weight ratio of silicone to film-forming polymer is from about 10:1 to about 1:10, preferably from about 5:1 to about 1:5, and more preferably from about 2:1 to about 1:2. Typically, the preferred wrinkle reducing active of silicone plus polymer is present at a level of from about 0.1% to about 8%, preferably from about 0.3% to about 5%, more preferably from about 0.5% to about 3%, by weight of the composition.

Other preferred adhesive and/or film forming polymers that are useful in the composition of the present invention actually contain silicone moieties in the polymers themselves, typically present as block and/or graft copolymers.

When the optional cyclodextrin is present in the composition, the polymer useful in providing shape retention in the composition of the present invention should be cyclodextrin-compatible, that is it should not substantially form complexes with

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cyclodextrin so as to diminish performance of the cyclodextrin and/or the polymer. Complex formation affects both the ability of the cyclodextrin to absorb odors and the ability of the polymer to impart shape retention to fabric. In this case, the monomers having pendant groups that can complex with cyclodextrin are not preferred because they can form complexes with cyclodextrin. Examples of such monomers are acrylic or methacrylic acid esters of C7-C18 alcohols, such as neodecanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, and 1-decanol; aromatic vinyls, such as styrene; t-butylstyrene; vinyl toluene; and the like.

Starch

Starch is not normally preferred, since it makes the fabric resistant to deformation. However, it does provide increased "body" which is often desired. Starch is particularly preferred in compositions of this invention to be used with ironing. When used, starch is solubilized or dispersed in the composition. Any type of starch, e.g. those derived from corn, wheat, rice, grain sorghum, waxy grain sorghum, waxy maize or tapioca, or mixtures thereof and water soluble or dispersible modifications or derivatives thereof, can be used in the composition of the present invention. Modified starches that can be used include natural starches that have been degraded to obtain a lower viscosity by acidic, oxidative or enzymatic depolymerization. Additionally, low viscosity commercially available propoxylated and/or ethoxylated starches are useable in the present composition and are preferred since their low viscosity at relatively high solids concentrations make them very adaptable to spraying processes. Suitable alkoxyated, low viscosity starches are submicron sized particles of hydrophobic starch that are readily dispersed in water and are prepared by alkoxylation of granular starch with a monofunctional alkoxyating agent which provides the starch with ether linked hydrophilic groups. A suitable method for their preparation is taught in U.S. Pat. No. 3,462,283. In accordance with the invention, the propoxylated or ethoxylated starch derivatives are dispersed in the aqueous medium in an amount of from about 0.1% to about 10%, preferably from about 0.5% to about 6%, more preferably from about 1% to about 4% by weight of the usage composition.

Preferred pH Range

Compositions according to the present invention, which contain a shape retention polymer having hydrophilic monomers with an acid functional pending group, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and mixtures thereof, preferably are adjusted to have a pH of greater than about 6, preferably from about 7 and about 11, more preferably from about 8 to about 10.5, most

preferably from about 9 to about 10.5 to improve the solubility of the polymer. Above pH 11, the ability of cyclodextrin, when present, to form complexes and to control odor is diminished. This is achieved by the addition of a caustic alkali. Example of suitable caustic alkalis for use herein include sodium and potassium hydroxides.

These polymers, by themselves, also provide odor control to some amine type malodors. If amine malodor control is desired, the pH of the solution should be kept as low as possible, preferably from about 6 to about 8, more preferably from about 6.5 to about 7.5.

(3) Lithium Salts.

Lithium salts are disclosed to be used as solubilizing aids in the production silk fibroin using lithium bromide, e.g., U.S. Pat. No. 4,233,212, issued Nov. 11, 1980 to Otoi et al., and lithium thiocyanate, e.g., U.S. Pat. No. 5,252,285, issued Oct. 12, 1993 to Robert L. Lock. U.S. Pat. No. 5,296,269, issued Mar. 22, 1994 to Yang et al. discloses a process to produce crease-resistant silk using lithium bromide and lithium chloride. U.S. Pat. No. 5,199,954, issued Apr. 6, 1993 to Schultz et al. discloses a hair dye composition containing lithium bromide. U.S. Pat. No. 5,609,859, issued Mar. 11, 1997 to D. R. Cowsar discloses methods for preparing hair relaxer creams containing a lithium salt. Lithium salts are disclosed as static control agents in a liquid softener composition in U.S. Pat. No. 4,069,159, issued Jan. 17, 1978 to Mason Hayek. All of these patents are incorporated herein by reference.

It is now found that aqueous compositions comprising lithium salts provide improved fabric wrinkle control. Nonlimiting examples of lithium salts that are useful in the present invention are lithium bromide, lithium chloride, lithium lactate, lithium benzoate, lithium acetate, lithium sulfate, lithium tartrate, and/or lithium bitartrate, preferably lithium bromide and/or lithium lactate. Some water soluble salts such as , lithium benzoate are not preferred when the optional cyclodextrin is present because they can form complexes with cyclodextrin. Useful levels of lithium salts are from about 0.1% to about 10%, preferably from about 0.5% to about 7%, more preferably from about 1% to about 5%, by weight of the usage composition.

(4) Optional Hydrophilic Plasticizer

Optionally, the composition can contain a hydrophilic plasticizer to soften both the fabric fibers, especially cotton fibers, and the adhesive and/or film-forming shape retention polymers. Examples of the preferred hydrophilic plasticizers are short chain low molecular weight polyhydric alcohols, such as is glycerol, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, sorbitol, erythritol or mixtures thereof, more preferably diethylene glycol, dipropylene glycol, ethylene glycol,

propylene glycol and mixtures thereof. When cyclodextrin is present, the plasticizer should be compatible with it.

The aqueous compositions containing these plasticizers also tend to provide a slower drying profile for clothing/fabrics, to allow time for any wrinkles to disappear when the clothing/fabrics are hung to dry. This is balanced by the desire by most consumer to have the garments to dry faster. Therefore, when needed, the plasticizers should be used at an effective, but as low as possible, level in the composition. When a hydrophilic plasticizer is used, it is present in the at a level of from 0.01% to 5%, preferably from 0.05% to 2%, more preferably from 0.1% to 1% by weight of the usage composition.

(5) Mixtures thereof.

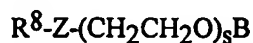
As stated hereinbefore, the composition can also contain mixtures of fiber lubricant, shape retention polymer, plasticizer, and lithium salts.

OPTIONAL INGREDIENTS

(1). Surfactant

Surfactant is an optional but highly preferred ingredient of the present invention. Surfactant is especially useful in the composition to facilitate the dispersion and/or solubilization of wrinkle control agents such as silicones and/or certain relatively water insoluble shape retention polymers. The surfactant can provide some plasticizing effect to the shape retention polymers resulting in a more flexible polymer network. Surfactant can provide a low surface tension that permits the composition to spread readily and more uniformly on hydrophobic surfaces like polyester and nylon. Such surfactant is preferably included when the composition is used in a spray dispenser in order to enhance the spray characteristics of the composition and allow the composition to distribute more evenly, and to prevent clogging of the spray apparatus. The spreading of the composition can also allow it to dry faster, so that the treated material is ready to use sooner. For concentrated compositions, the surfactant facilitates the dispersion of many actives such as antimicrobial actives and perfumes in the concentrated aqueous compositions. Suitable surfactant useful in the present invention is nonionic surfactant, anionic surfactant, cationic surfactant, amphoteric surfactant, and mixtures thereof. When surfactant is used in the composition of the present invention, it is added at an effective amount to provide one, or more of the benefits described herein, typically from about 0.01% to about 5%, preferably from about 0.05% to about 3%, more preferably from about 0.1% to about 2%, and even more preferably, from about 0.2% to about 1%, by weight of the usage composition.

A preferred type of surfactant is ethoxylated surfactant, such as addition products of ethylene oxide with fatty alcohols, fatty acids, fatty amines, etc. Optionally, addition products of mixtures of ethylene oxide and propylene oxide with fatty alcohols, fatty acids, fatty amines may be used. The ethoxylated surfactant includes compounds having the general formula:



wherein R^8 is an alkyl group or an alkyl aryl group, selected from the group consisting of primary, secondary and branched chain alkyl hydrocarbyl groups, primary, secondary and branched chain alkenyl hydrocarbyl groups, and/or primary, secondary and branched chain alkyl- and alkenyl-substituted phenolic hydrocarbyl groups having from about 6 to about 20 carbon atoms, preferably from about 8 to about 18, more preferably from about 10 to about 15 carbon atoms; s is an integer from about 2 to about 45, preferably from about 2 to about 20, more preferably from about 2 to about 15; B is a hydrogen, a carboxylate group, or a sulfate group; and linking group Z is $-O-$, $-C(O)O-$, $-C(O)N(R)-$, or $-C(O)N(R)-$, and mixtures thereof, in which R , when present, is R^8 or hydrogen.

The nonionic surfactants herein are characterized by an HLB (hydrophilic-lipophilic balance) of from 5 to 20, preferably from 6 to 15.

Nonlimiting examples of preferred ethoxylated surfactant are:

- straight-chain, primary alcohol ethoxylates, with R^8 being C_8-C_{18} alkyl and/or alkenyl group, more preferably $C_{10}-C_{14}$, and s being from about 2 to about 8, preferably from about 2 to about 6;
- straight-chain, secondary alcohol ethoxylates, with R^8 being C_8-C_{18} alkyl and/or alkenyl, e.g., 3-hexadecyl, 2-octadecyl, 4-eicosanyl, and 5-eicosanyl, and s being from about 2 to about 10;
- alkyl phenol ethoxylates wherein the alkyl phenols having an alkyl or alkenyl group containing from 3 to 20 carbon atoms in a primary, secondary or branched chain configuration, preferably from 6 to 12 carbon atoms, and s is from about 2 to about 12, preferably from about 2 to about 8;
- branched chain alcohol ethoxylates, wherein branched chain primary and secondary alcohols (or Guerbet alcohols) which are available, e.g., from the well-known "OXO" process or modification thereof are ethoxylated.

Especially preferred are alkyl ethoxylate surfactants with each R^8 being C_8-C_{16} straight chain and/or branch chain alkyl and the number of ethyleneoxy groups s being from about 2 to about 6, preferably from about 2 to about 4, more preferably with R^8 being C_8-C_{15} alkyl and s being from about 2.25 to about 3.5. These nonionic surfactants are characterized by an HLB of from 6 to about 11, preferably from about 6.5 to about

9.5, and more preferably from about 7 to about 9. Nonlimiting examples of commercially available preferred surfactants are Neodol 91-2.5 (C_9-C_{10} , $s = 2.7$, HLB = 8.5), Neodol 23-3 ($C_{12}-C_{13}$, $s = 2.9$, HLB = 7.9) and Neodol 25-3 ($C_{12}-C_{15}$, $s = 2.8$, HLB = 7.5). It is found, very surprisingly, that these preferred surfactants which are themselves not very water soluble (0.1% aqueous solutions of these surfactants are not clear), can at low levels, effectively dissolve and/or disperse shape retention polymers such as copolymers containing acrylic acid and tert-butyl acrylate into clear compositions, even without the presence of a low molecular weight alcohol.

Other examples of preferred ethoxylated surfactant include carboxylated alcohol ethoxylate, also known as ether carboxylate, with R^8 having from about 12 to about 16 carbon atoms and s being from about 5 to about 13; ethoxylated quaternary ammonium surfactants, such as PEG-5 cocomonium methosulfate, PEG-15 cocomonium chloride, PEG-15 oleammonium chloride and bis(polyethoxyethanol)tallow ammonium chloride;

Other suitable nonionic ethoxylated surfactants are ethoxylated alkyl amines derived from the condensation of ethylene oxide with hydrophobic alkyl amines, with R^8 having from about 8 to about 22 carbon atoms and s being from about 3 to about 30.

Cyclodextrin-Compatible Surfactant

When the optional cyclodextrin is present, the surfactant for use in providing the required low surface tension in the composition of the present invention should be cyclodextrin-compatible, that is it should not substantially form a complex with the cyclodextrin so as to diminish performance of the cyclodextrin and/or the surfactant when cyclodextrin is present. Complex formation diminishes both the ability of the cyclodextrin to absorb odors and the ability of the surfactant to lower the surface tension of the aqueous composition.

Suitable cyclodextrin-compatible surfactants can be readily identified by the absence of effect of cyclodextrin on the surface tension provided by the surfactant. This is achieved by determining the surface tension (in dyne/cm²) of aqueous solutions of the surfactant in the presence and in the absence of about 1% of a specific cyclodextrin in the solutions. The aqueous solutions contain surfactant at concentrations of approximately 0.5%, 0.1%, 0.01%, and 0.005%. The cyclodextrin can affect the surface activity of a surfactant by elevating the surface tension of the surfactant solution. If the surface tension at a given concentration in water differs by more than about 10% from the surface tension of the same surfactant in the 1% solution of the cyclodextrin, that is an indication of a strong interaction between the surfactant and the cyclodextrin. The preferred surfactants herein should have a surface tension in an aqueous solution that is different (lower) by less than about 10%, preferably less than about 5%, and more

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preferably less than about 1% from that of the same concentration solution containing 1% cyclodextrin.

Nonlimiting examples of cyclodextrin-compatible nonionic surfactants include block copolymers of ethylene oxide and propylene oxide. Suitable block polyoxyethylene-polyoxypropylene polymeric surfactants, that are compatible with most cyclodextrins, include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as the initial reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initial compounds with a single reactive hydrogen atom, such as C₁₂₋₁₈ aliphatic alcohols, are not generally compatible with the cyclodextrin. Certain of the block polymer surfactant compounds designated Pluronic[®] and Tetronic[®] by the BASF-Wyandotte Corp., Wyandotte, Michigan, are readily available.

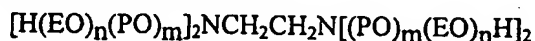
Nonlimiting examples of cyclodextrin-compatible surfactants of this type include:

Pluronic Surfactants with the general formula $H(EO)_n(PO)_m(EO)_nH$, wherein EO is an ethylene oxide group, PO is a propylene oxide group, and n and m are numbers that indicate the average number of the groups in the surfactants. Typical examples of cyclodextrin-compatible Pluronic surfactants are:

Name	Average MW	Average n	Average m
L-101	3,800	4	59
L-81	2,750	3	42
L-44	2,200	10	23
L-43	1,850	6	22
F-38	4,700	43	16
P-84	4,200	19	43,

and mixtures thereof.

Tetronic Surfactants with the general formula:



wherein EO, PO, n, and m have the same meanings as above. Typical examples of cyclodextrin-compatible Tetronic surfactants are:

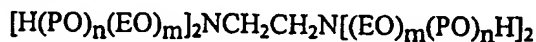
Name	Average MW	Average n	Average m
901	4,700	3	18
908	25,000	114	22,

and mixtures thereof.

"Reverse" Pluronic and Tetronic surfactants have the following general formulas:

Reverse Pluronic Surfactants $H(PO)_m(EO)_n(PO)_mH$

Reverse Tetronic Surfactants



wherein EO, PO, n, and m have the same meanings as above. Typical examples of cyclodextrin-compatible Reverse Pluronic and Reverse Tetronic surfactants are:

Reverse Pluronic surfactants:

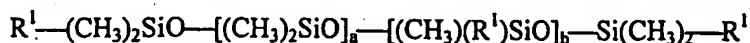
Name	Average MW	Average n	Average m
10 R5	1,950	8	22
25 R1	2,700	21	6

Reverse Tetronic surfactants

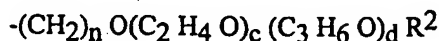
Name	Average MW	Average n	Average m
130 R2	7,740	9	26
70 R2	3,870	4	13

and mixtures thereof.

A preferred class of cyclodextrin-compatible nonionic surfactants are the polyalkylene oxide polysiloxanes having a dimethyl polysiloxane hydrophobic moiety and one or more hydrophilic polyalkylene side chains, and having the general formula:



wherein $a + b$ are from about 1 to about 50, preferably from about 3 to about 30, more preferably from about 10 to about 25, and each R^1 is the same or different and is selected from the group consisting of methyl and a poly(ethyleneoxide/propyleneoxide) copolymer group having the general formula:



with at least one R^1 being a poly(ethyleneoxy/propyleneoxy) copolymer group, and wherein n is 3 or 4, preferably 3; total c (for all polyalkyleneoxy side groups) has a value of from 1 to about 100, preferably from about 6 to about 100; total d is from 0 to about 14, preferably from 0 to about 3; and more preferably d is 0; total $c+d$ has a value of from about 5 to about 150, preferably from about 9 to about 100 and each R^2 is the same or different and is selected from the group consisting of hydrogen, an alkyl having 1 to 4 carbon atoms, and an acetyl group, preferably hydrogen and methyl group. Each polyalkylene oxide polysiloxane has at least one R^1 group being a poly(ethyleneoxide/propyleneoxide) copolymer group.

Nonlimiting examples of this type of surfactants are the Silwet[®] surfactants which are available OSi Specialties, Inc., Danbury, Connecticut. Representative Silwet surfactants which contain only ethyleneoxy (C_2H_4O) groups are as follows.

Name	Average MW	Average a+b	Average total c
L-7608	600	1	9
L-7607	1,000	2	17
L-77	600	1	9
L-7605	6,000	20	99
L-7604	4,000	21	53
L-7600	4,000	11	68
L-7657	5,000	20	76
L-7602	3,000	20	29
L-7622	10,000	88	75

Nonlimiting examples of surfactants which contain both ethyleneoxy ($C_2 H_4 O$) and propyleneoxy ($C_3 H_6 O$) groups are as follows.

Name	Average MW	EO/PO ratio
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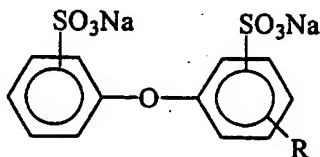
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Silwet L-720	12,000	50/50
Silwet L-7001	20,000	40/60
Silwet L-7002	8,000	50/50
Silwet L-7210	13,000	20/80
Silwet L-7200	19,000	75/25
Silwet L-7220	17,000	20/80

The molecular weight of the polyalkyleneoxy group (R^1) is less than or equal to about 10,000. Preferably, the molecular weight of the polyalkyleneoxy group is less than or equal to about 8,000, and most preferably ranges from about 300 to about 5,000. Thus, the values of c and d can be those numbers which provide molecular weights within these ranges. However, the number of ethyleneoxy units ($-C_2H_4O$) in the polyether chain (R^1) must be sufficient to render the polyalkylene oxide polysiloxane water dispersible or water soluble. If propyleneoxy groups are present in the polyalkyleneoxy chain, they can be distributed randomly in the chain or exist as blocks. Surfactants which contain only propyleneoxy groups without ethyleneoxy groups are not preferred. Preferred Silwet surfactants are L-7600, L-7602, L-7604, L-7605, L-7657, and mixtures thereof. Besides surface activity, polyalkylene oxide polysiloxane surfactants can also provide other benefits, such as antistatic benefits, lubricity and softness to fabrics.

The preparation of polyalkylene oxide polysiloxanes is well known in the art. Polyalkylene oxide polysiloxanes of the present invention can be prepared according to the procedure set forth in U.S. Pat. No. 3,299,112, incorporated herein by reference. Typically, polyalkylene oxide polysiloxanes of the surfactant blend of the present invention are readily prepared by an addition reaction between a hydrosiloxane (i.e., a siloxane containing silicon-bonded hydrogen) and an alkenyl ether (e.g., a vinyl, allyl, or methallyl ether) of an alkoxy or hydroxy end-blocked polyalkylene oxide). The reaction conditions employed in addition reactions of this type are well known in the art and in general involve heating the reactants (e.g., at a temperature of from about 85° C. to 110° C.) in the presence of a platinum catalyst (e.g., chloroplatinic acid) and a solvent (e.g., toluene).

Nonlimiting examples of cyclodextrin-compatible anionic surfactants are the alkyldiphenyl oxide disulfonate, having the general formula:



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wherein R is an alkyl group. Examples of this type of surfactants are available from the Dow Chemical Company under the trade name Dowfax® wherein R is a linear or branched C₆-C₁₆ alkyl group. An example of these cyclodextrin-compatible anionic surfactant is Dowfax 3B2 with R being approximately a linear C₁₀ group. These anionic surfactants are preferably not used when the antimicrobial active or preservative, etc., is cationic to minimize the interaction with the cationic actives, since the effect of both surfactant and active are diminished.

The surfactants above are either weakly interactive with cyclodextrin (less than 5% elevation in surface tension, or non-interactive (less than 1% elevation in surface tension). Normal surfactants like sodium dodecyl sulfate and dodecanolpoly(6)ethoxylate are strongly interactive, with more than a 10% elevation in surface tension in the presence of a typical cyclodextrin like hydroxypropyl-beta-cyclodextrin and methylated beta-cyclodextrin.

Typical levels of cyclodextrin-compatible surfactants in usage compositions are from about 0.01% to about 2%, preferably from about 0.03% to about 0.6%, more preferably from about 0.05% to about 0.3%, by weight of the composition. Typical levels of cyclodextrin-compatible surfactants in concentrated compositions are from about 0.1% to about 8%, preferably from about 0.2% to about 4%, more preferably from about 0.3% to about 3%, by weight of the concentrated composition.

(2). Odor Control Agent

The compositions for odor control are of the type disclosed in U.S. Pats. 5,534,165; 5,578,563; 5,663,134; 5,668,097; 5,670,475; and 5,714,137, Trinh et al. issued Jul. 9, 1996; Nov. 26, 1996; Sep. 2, 1997; Sep. 16, 1997; Sep. 23, 1997; and Feb. 3, 1998 respectively, all of said patents being incorporated herein by reference. Such compositions can contain several different odor control agents in addition to the polymers described hereinbefore that can control amine odors.

(a). Cyclodextrin

As used herein, the term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in donut-shaped rings. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structures with hollow interiors of specific volumes. The "lining" of each internal cavity

is formed by hydrogen atoms and glycosidic bridging oxygen atoms; therefore, this surface is fairly hydrophobic. The unique shape and physical-chemical properties of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes with) organic molecules or parts of organic molecules which can fit into the cavity. Many odorous molecules can fit into the cavity including many malodorous molecules and perfume molecules. Therefore, cyclodextrins, and especially mixtures of cyclodextrins with different size cavities, can be used to control odors caused by a broad spectrum of organic odoriferous materials, which may, or may not, contain reactive functional groups. The complexation between cyclodextrin and odorous molecules occurs rapidly in the presence of water. However, the extent of the complex formation also depends on the polarity of the absorbed molecules. In an aqueous solution, strongly hydrophilic molecules (those which are highly water-soluble) are only partially absorbed, if at all. Therefore, cyclodextrin does not complex effectively with some very low molecular weight organic amines and acids when they are present at low levels on wet fabrics. As the water is being removed however, e.g., the fabric is being dried off, some low molecular weight organic amines and acids have more affinity and will complex with the cyclodextrins more readily.

The cavities within the cyclodextrin in the solution of the present invention should remain essentially unfilled (the cyclodextrin remains uncomplexed) while in solution, in order to allow the cyclodextrin to absorb various odor molecules when the solution is applied to a surface. Non-derivatised (normal) beta-cyclodextrin can be present at a level up to its solubility limit of about 1.85% (about 1.85g in 100 grams of water) at room temperature. Beta-cyclodextrin is not preferred in compositions which call for a level of cyclodextrin higher than its water solubility limit. Non-derivatised beta-cyclodextrin is generally not preferred when the composition contains surfactant since it affects the surface activity of most of the preferred surfactants that are compatible with the derivatised cyclodextrins.

Preferably, the odor absorbing solution of the present invention is clear. The term "clear" as defined herein means transparent or translucent, preferably transparent, as in "water clear," when observed through a layer having a thickness of less than about 10 cm.

Preferably, the cyclodextrins used in the present invention are highly water-soluble such as, alpha-cyclodextrin and/or derivatives thereof, gamma-cyclodextrin and/or derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. The derivatives of cyclodextrin consist mainly of molecules wherein some of the OH groups are converted to OR groups. Cyclodextrin derivatives include, e.g., those with short

chain alkyl groups such as methylated cyclodextrins, and ethylated cyclodextrins, wherein R is a methyl or an ethyl group; those with hydroxyalkyl substituted groups, such as hydroxypropyl cyclodextrins and/or hydroxyethyl cyclodextrins, wherein R is a $\text{-CH}_2\text{-CH(OH)-CH}_3$ or a $\text{-CH}_2\text{CH}_2\text{-OH}$ group; branched cyclodextrins such as maltose-bonded cyclodextrins; cationic cyclodextrins such as those containing 2-hydroxy-3-(dimethylamino)propyl ether, wherein R is $\text{CH}_2\text{-CH(OH)-CH}_2\text{-N(CH}_3)_2$ which is cationic at low pH; quaternary ammonium, e.g., 2-hydroxy-3-(trimethylammonio)propyl ether chloride groups, wherein R is $\text{CH}_2\text{-CH(OH)-CH}_2\text{-N}^+(\text{CH}_3)_3\text{Cl}^-$; anionic cyclodextrins such as carboxymethyl cyclodextrins, cyclodextrin sulfates, and cyclodextrin succinylates; amphoteric cyclodextrins such as carboxymethyl/quaternary ammonium cyclodextrins; cyclodextrins wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure, e.g., the mono-3-6-anhydrocyclodextrins, as disclosed in "Optimal Performances with Minimal Chemical Modification of Cyclodextrins", F. Diedaini-Pilard and B. Perly, The 7th International Cyclodextrin Symposium Abstracts, April 1994, p. 49, said references being incorporated herein by reference; and mixtures thereof. Other cyclodextrin derivatives are disclosed in U.S. Pat. Nos.: 3,426,011, Parmerter et al., issued Feb. 4, 1969; 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued July 1, 1969; 3,459,731, Gramera et al., issued Aug. 5, 1969; 3,553,191, Parmerter et al., issued Jan. 5, 1971; 3,565,887, Parmerter et al., issued Feb. 23, 1971; 4,535,152, Szejtli et al., issued Aug. 13, 1985; 4,616,008, Hirai et al., issued Oct. 7, 1986; 4,678,598, Ogino et al., issued Jul. 7, 1987; 4,638,058, Brandt et al., issued Jan. 20, 1987; and 4,746,734, Tsuchiyama et al., issued May 24, 1988; all of said patents being incorporated herein by reference.

Highly water-soluble cyclodextrins are those having water solubility of at least about 10 g in 100 ml of water at room temperature, preferably at least about 20 g in 100 ml of water, more preferably at least about 25 g in 100 ml of water at room temperature. The availability of solubilized, uncomplexed cyclodextrins is essential for effective and efficient odor control performance. Solubilized, water-soluble cyclodextrin can exhibit more efficient odor control performance than non-water-soluble cyclodextrin when deposited onto surfaces, especially fabric.

Examples of preferred water-soluble cyclodextrin derivatives suitable for use herein are hydroxypropyl alpha-cyclodextrin, methylated alpha-cyclodextrin, methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and hydroxypropyl beta-cyclodextrin. Hydroxyalkyl cyclodextrin derivatives preferably have a degree of substitution of from about 1 to about 14, more preferably from about 1.5 to about 7, wherein the total number of OR groups per cyclodextrin is defined as the degree of substitution. Methylated

cyclodextrin derivatives typically have a degree of substitution of from about 1 to about 18, preferably from about 3 to about 16. A known methylated beta-cyclodextrin is heptakis-2,6-di-O-methyl- β -cyclodextrin, commonly known as DIMEB, in which each glucose unit has about 2 methyl groups with a degree of substitution of about 14. A preferred, more commercially available, methylated beta-cyclodextrin is a randomly methylated beta-cyclodextrin, commonly known as RAMEB, having different degrees of substitution, normally of about 12.6. RAMEB is more preferred than DIMEB, since DIMEB affects the surface activity of the preferred surfactants more than RAMEB. The preferred cyclodextrins are available, e.g., from Cerestar USA, Inc. and Wacker Chemicals (USA), Inc.

It is also preferable to use a mixture of cyclodextrins. Such mixtures absorb odors more broadly by complexing with a wider range of odoriferous molecules having a wider range of molecular sizes. Preferably at least a portion of the cyclodextrins is alpha-cyclodextrin and its derivatives thereof, gamma-cyclodextrin and its derivatives thereof, and/or derivatised beta-cyclodextrin, more preferably a mixture of alpha-cyclodextrin, or an alpha-cyclodextrin derivative, and derivatised beta-cyclodextrin, even more preferably a mixture of derivatised alpha-cyclodextrin and derivatised beta-cyclodextrin, most preferably a mixture of hydroxypropyl alpha-cyclodextrin and hydroxypropyl beta-cyclodextrin, and/or a mixture of methylated alpha-cyclodextrin and methylated beta-cyclodextrin.

For controlling odor on fabrics, the composition is preferably used as a spray. It is preferable that the usage compositions of the present invention contain low levels of cyclodextrin so that a visible stain does not appear on the fabric at normal usage levels. Preferably, the solution used to treat the surface under usage conditions is virtually not discernible when dry. Typical levels of cyclodextrin in usage compositions for usage conditions are from about 0.01% to about 5%, preferably from about 0.1% to about 4%, more preferably from about 0.5% to about 2% by weight of the composition. Compositions with higher concentrations can leave unacceptable visible stains on fabrics as the solution evaporates off of the fabric. This is especially a problem on thin, colored, synthetic fabrics. In order to avoid or minimize the occurrence of fabric staining, it is preferable that the fabric be treated at a level of less than about 5 mg of cyclodextrin per gram of fabric, more preferably less than about 2 mg of cyclodextrin per gram of fabric. The presence of the surfactant can improve appearance by minimizing localized spotting.

Concentrated compositions can also be used in order to deliver a less expensive product. When a concentrated product is used, i.e., when the level of cyclodextrin used is from about 3% to about 20%, more preferably from about 5% to about 10%, by weight

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of the concentrated composition, it is preferable to dilute the concentrated composition before treating fabrics in order to avoid staining. Preferably the concentrated cyclodextrin composition is diluted with about 50% to about 6000%, more preferably with about 75% to about 2000%, most preferably with about 100% to about 1000% by weight of the concentrated composition of water. The resulting diluted compositions have usage concentrations of cyclodextrin as discussed hereinbefore, e.g., of from about 0.1% to about 5%, by weight of the diluted composition.

(b). Metal Salts

Optionally, but highly preferred, the present invention can include metallic salts for added odor absorption and/or antimicrobial benefit for the cyclodextrin solution when cyclodextrin is present. The metallic salts are selected from the group consisting of copper salts, zinc salts, and mixtures thereof.

Copper salts have some antimicrobial benefits. Specifically, cupric abietate acts as a fungicide, copper acetate acts as a mildew inhibitor, cupric chloride acts as a fungicide, copper lactate acts as a fungicide, and copper sulfate acts as a germicide. Copper salts also possess some malodor control abilities. See U. S. Pat. No. 3,172,817, Leupold, et al., which discloses deodorizing compositions for treating disposable articles, comprising at least slightly water-soluble salts of acylacetone, including copper salts and zinc salts, all of said patents are incorporated herein by reference.

The preferred zinc salts possess malodor control abilities. Zinc has been used most often for its ability to ameliorate malodor, e.g., in mouth wash products, as disclosed in U.S. Pat. Nos. 4,325,939, issued Apr. 20, 1982 and 4,469,674, issued Sept. 4, 1983, to N. B. Shah, et al., all of which are incorporated herein by reference. Highly-ionized and soluble zinc salts such as zinc chloride, provide the best source of zinc ions. Zinc borate functions as a fungistat and a mildew inhibitor, zinc caprylate functions as a fungicide, zinc chloride provides antiseptic and deodorant benefits, zinc ricinoleate functions as a fungicide, zinc sulfate heptahydrate functions as a fungicide and zinc undecylenate functions as a fungistat.

Preferably the metallic salts are water-soluble zinc salts, copper salts or mixtures thereof, and more preferably zinc salts, especially ZnCl_2 . These salts are preferably present in the present invention primarily to absorb amine and sulfur-containing compounds that have molecular sizes too small to be effectively complexed with the cyclodextrin molecules. Low molecular weight sulfur-containing materials, e.g., sulfide and mercaptans, are components of many types of malodors, e.g., food odors (garlic, onion), body/perspiration odor, breath odor, etc. Low molecular weight amines are also components of many malodors, e.g., food odors, body odors, urine, etc.

When metallic salts are added to the composition of the present invention they are typically present at a level of from about 0.1% to about 10%, preferably from about 0.2% to about 8%, more preferably from about 0.3% to about 5% by weight of the usage composition. When zinc salts are used as the metallic salt, and a clear solution is desired, it is preferable that the pH of the solution is adjusted to less than about 7, more preferably less than about 6, most preferably, less than about 5, in order to keep the solution clear.

(c). Soluble Carbonate and/or Bicarbonate Salts

Water-soluble alkali metal carbonate and/or bicarbonate salts, such as sodium bicarbonate, potassium bicarbonate, potassium carbonate, cesium carbonate, sodium carbonate, and mixtures thereof can be added to the composition of the present invention in order to help to control certain acid-type odors. Preferred salts are sodium carbonate monohydrate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, and mixtures thereof. When these salts are added to the composition of the present invention, they are typically present at a level of from about 0.1% to about 5%, preferably from about 0.2% to about 3%, more preferably from about 0.3% to about 2%, by weight of the composition. When these salts are added to the composition of the present invention it is preferably that incompatible metal salts not be present in the invention. Preferably, when these salts are used the composition should be essentially free of zinc and other incompatible metal ions, e.g., Ca, Fe, Ba, etc. which form water-insoluble salts.

(d). Enzymes

Enzymes can be used to control certain types of malodor, especially malodor from urine and other types of excretions, including regurgitated materials. Proteases are especially desirable. The activity of commercial enzymes depends very much on the type and purity of the enzyme being considered. Enzymes that are water soluble proteases like pepsin, trypsin, ficin, bromelin, papain, rennin, and mixtures thereof are particularly useful.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, preferably from about 0.001 mg to about 3 mg, more preferably from about 0.002 mg to about 1 mg, of active enzyme per gram of the aqueous compositions. Stated otherwise, the aqueous compositions herein can comprise from about 0.0001% to about 0.5%, preferably from about 0.001% to about 0.3%, more preferably from about 0.005% to about 0.2% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.0005 to 0.1 Anson units (AU) of activity per gram of aqueous composition.

Nonlimiting examples of suitable, commercially available, water soluble proteases are pepsin, trypsin, ficin, bromelin, papain, rennin, and mixtures thereof. Papain can be isolated, e.g., from papaya latex, and is available commercially in the purified form of up to, e.g., about 80% protein, or cruder, technical grade of much lower activity. Other suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the trade names ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985); Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985); and proteases made by Genencor International, Inc., according to one or more of the following patents: Caldwell et al, U.S. Patent Nos. 5,185,258, 5,204,015 and 5,244,791.

A wide range of enzyme materials and means for their incorporation into liquid compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985. Other enzyme materials useful for liquid formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes can be stabilized by various techniques, e.g., those disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al., European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas, and in U.S. Patent 3,519,570. All of the above patents and applications are incorporated herein, at least in pertinent part.

Enzyme-polyethylene glycol conjugates are also preferred. Such polyethylene glycol (PEG) derivatives of enzymes, wherein the PEG or alkoxy-PEG moieties are coupled to the protein molecule through, e.g., secondary amine linkages. Suitable derivatization decreases immunogenicity, thus minimizes allergic reactions, while still maintaining some enzymatic activity. An example of protease-PEG's is PEG-subtilisin

Carlsberg from *B. lichenniformis* coupled to methoxy-PEGs through secondary amine linkage, and is available from Sigma-Aldrich Corp., St. Louis, Missouri.

(e). Zeolites

When the clarity of the solution is not needed, and the solution is not sprayed on fabrics, other optional odor absorbing materials, e.g., zeolites and/or activated carbon, can also be used. A preferred class of zeolites is characterized as "intermediate" silicate/aluminate zeolites. The intermediate zeolites are characterized by $\text{SiO}_2/\text{AlO}_2$ molar ratios of less than about 10. Preferably the molar ratio of $\text{SiO}_2/\text{AlO}_2$ ranges from about 2 to about 10. The intermediate zeolites have an advantage over the "high" zeolites. The intermediate zeolites have a higher affinity for amine-type odors, they are more weight efficient for odor absorption because they have a larger surface area, and they are more moisture tolerant and retain more of their odor absorbing capacity in water than the high zeolites. A wide variety of intermediate zeolites suitable for use herein are commercially available as Valfor[®] CP301-68, Valfor[®] 300-63, Valfor[®] CP300-35, and Valfor[®] CP300-56, available from PQ Corporation, and the CBV100[®] series of zeolites from Conteka.

Zeolite materials marketed under the trade name Abscents[®] and Smellrite[®], available from The Union Carbide Corporation and UOP are also preferred. These materials are typically available as a white powder in the 3-5 micron particle size range. Such materials are preferred over the intermediate zeolites for control of sulfur-containing odors, e.g., thiols, mercaptans.

(f). Activated Carbon

The carbon material suitable for use in the present invention is the material well known in commercial practice as an absorbent for organic molecules and/or for air purification purposes. Often, such carbon material is referred to as "activated" carbon or "activated" charcoal. Such carbon is available from commercial sources under such trade names as; Calgon-Type CPG[®]; Type PCB[®]; Type SGL[®]; Type CAL[®]; and Type OL[®].

(g). Mixtures Thereof

Mixtures of the above materials are desirable, especially when the mixture provides control over a broader range of odors.

(E). PERFUME

The wrinkle control composition of the present invention can also optionally provide a "scent signal" in the form of a pleasant odor which provides a freshness impression to the treated fabrics. The scent signal can be designed to provide a fleeting perfume scent. When perfume is added as a scent signal, it is added only at very low levels, e.g., from about 0% to about 0.5%, preferably from about 0.003% to about 0.3%, more preferably from about 0.005% to about 0.2%, by weight of the usage composition.

Perfume can also be added as a more intense odor in product and on fabrics. When stronger levels of perfume are preferred, relatively higher levels of perfume can be added.

Any type of perfume can be incorporated into the composition of the present invention. The preferred perfume ingredients are those suitable for use to apply on fabrics and garments. Typical examples of such preferred ingredients are given in U.S. Pat. 5,445,747, issued Aug. 29, 1995 to Kvietok et al., incorporated herein by reference.

When long lasting fragrance odor on fabrics is desired, it is preferred to use at least an effective amount of perfume ingredients which have a boiling point of about 300°C or higher. Nonlimiting examples of such preferred ingredients are given in U.S. Pat. 5,500,138, issued Mar. 19, 1996 to Bacon et al., incorporated herein by reference. It is also preferred to use materials that can slowly release perfume ingredients after the fabric is treated by the wrinkle control composition of this invention. Examples of materials of this type are given in U.S. Pat. 5,531,910, Severns et al., issued July 2, 1996, said patent being incorporated herein by reference.

When cyclodextrin is present, it is essential that the perfume be added at a level wherein even if all of the perfume in the composition were to complex with the cyclodextrin molecules when cyclodextrin is present, there will still be an effective level of uncomplexed cyclodextrin molecules present in the solution to provide adequate odor control. In order to reserve an effective amount of cyclodextrin molecules for odor control when cyclodextrin is present, perfume is typically present at a level wherein less than about 90% of the cyclodextrin complexes with the perfume, preferably less than about 50% of the cyclodextrin complexes with the perfume, more preferably, less than about 30% of the cyclodextrin complexes with the perfume, and most preferably, less than about 10% of the cyclodextrin complexes with the perfume. The cyclodextrin to perfume weight ratio should be greater than about 8:1, preferably greater than about 10:1, more preferably greater than about 20:1, even more preferably greater than 40:1 and most preferably greater than about 70:1.

Preferably the perfume is hydrophilic and is composed predominantly of ingredients selected from two groups of ingredients, namely, (a) hydrophilic ingredients having a ClogP of less than about 3.5, more preferably less than about 3.0, and (b) ingredients having significant low detection threshold, and mixtures thereof. Typically, at least about 50%, preferably at least about 60%, more preferably at least about 70%, and most preferably at least about 80% by weight of the perfume is composed of perfume ingredients of the above groups (a) and (b). For these preferred perfumes, the cyclodextrin to perfume weight ratio is typically of from about 2:1 to about 200:1; preferably from about 4:1 to about 100:1, more preferably from about 6:1 to about 50:1, and even more preferably from about 8:1 to about 30:1.

(a). Hydrophilic Perfume Ingredients

The hydrophilic perfume ingredients are more soluble in water, have less of a tendency to complex with the cyclodextrins, and are more available in the odor absorbing composition than the ingredients of conventional perfumes. The degree of hydrophobicity of a perfume ingredient can be correlated with its octanol/water partition coefficient P. The octanol/water partition coefficient of a perfume ingredient is the ratio between its equilibrium concentration in octanol and in water. A perfume ingredient with a greater partition coefficient P is considered to be more hydrophobic. Conversely, a perfume ingredient with a smaller partition coefficient P is considered to be more hydrophilic. Since the partition coefficients of the perfume ingredients normally have high values, they are more conveniently given in the form of their logarithm to the base 10, logP. Thus the preferred perfume hydrophilic perfume ingredients of this invention have logP of about 3.5 or smaller, preferably of about 3.0 or smaller.

The logP of many perfume ingredients have been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), Irvine, California, contains many, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used

estimates for this physicochemical property, are used instead of the experimental logP values in the selection of perfume ingredients which are useful in the present invention.

Non-limiting examples of the more preferred hydrophilic perfume ingredients are allyl amyl glycolate, allyl caproate, amyl acetate, amyl propionate, anisic aldehyde, anisyl acetate, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl formate, benzyl iso valerate, benzyl propionate, beta gamma hexenol, calone, camphor gum, laevo-carveol, d-carvone, laevo-carvone, cinnamic alcohol, cinnamyl acetate, cinnamic alcohol, cinnamyl formate, cinnamyl propionate, cis-jasmone, cis-3-hexenyl acetate, coumarin, cuminic alcohol, cuminic aldehyde, Cyclal C, cyclogalbanate, dihydroeugenol, dihydro isojasmonate, dimethyl benzyl carbinol, dimethyl benzyl carbonyl acetate, ethyl acetate, ethyl aceto acetate, ethyl amyl ketone, ethyl anthranilate, ethyl benzoate, ethyl butyrate, ethyl cinnamate, ethyl hexyl ketone, ethyl maltol, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl phenyl acetate, ethyl salicylate, ethyl vanillin, eucalyptol, eugenol, eugenyl acetate, eugenyl formate, eugenyl methyl ether, fenchyl alcohol, flor acetate (tricyclo decenyl acetate), fructose, frutene (tricyclo decenyl propionate), geraniol, geranyl oxyacetaldehyde, heliotropin, hexenol, hexenyl acetate, hexyl acetate, hexyl formate, hinokitiol, hydrotropic alcohol, hydroxycitronellal, hydroxycitronellal diethyl acetal, hydroxycitronellol, indole, isoamyl alcohol, iso cyclo citral, isoeugenol, isoeugenyl acetate, isomenthone, isopulegyl acetate, isoquinoline, keone, ligustral, linalool, linalool oxide, linalyl formate, lyral, menthone, methyl acetophenone, methyl amyl ketone, methyl anthranilate, methyl benzoate, methyl benzyl acetate, methyl cinnamate, methyl dihydrojasmonate, methyl eugenol, methyl heptenone, methyl heptene carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl isobutenyl tetrahydropyran, methyl-N-methyl anthranilate, methyl beta naphthyl ketone, methyl phenyl carbonyl acetate, methyl salicylate, nerol, nonalactone, octalactone, octyl alcohol (octanol-2), para-anisic aldehyde, para-cresol, para-cresyl methyl ether, para hydroxy phenyl butanone, para-methoxy acetophenone, para-methyl acetophenone, phenoxy ethanol, phenoxyethyl propionate, phenyl acetaldehyde, phenylacetaldehyde diethyl ether, phenylethyl oxyacetaldehyde, phenyl ethyl acetate, phenyl ethyl alcohol, phenyl ethyl dimethyl carbinol, prenyl acetate, propyl butyrate, pulegone, rose oxide, safrole, terpineol, vanillin, viridine, and mixtures thereof.

Nonlimiting examples of other preferred hydrophilic perfume ingredients which can be used in perfume compositions of this invention are allyl heptoate, amyl benzoate, anethole, benzophenone, carvacrol, citral, citronellol, citronellyl nitrile, cyclohexyl ethyl acetate, cymal, 4-decenal, dihydro isojasmonate, dihydro myrcenol, ethyl methyl phenyl glycidate, fenchyl acetate, florhydral, gamma-nonolactone, geranyl formate, geranyl

nitrile, hexenyl isobutyrate, alpha-ionone, isobornyl acetate, isobutyl benzoate, isononyl alcohol, isomenthol, para-isopropyl phenylacetaldehyde, isopulegol, linalyl acetate, 2-methoxy naphthalene, menthyl acetate, methyl chavicol, musk ketone, beta naphthol methyl ether, neral, nonyl aldehyde, phenyl heptanol, phenyl hexanol, terpinyl acetate, Veratrol, yara-yara, and mixtures thereof.

The preferred perfume compositions used in the present invention contain at least 4 different hydrophilic perfume ingredients, preferably at least 5 different hydrophilic perfume ingredients, more preferably at least 6 different hydrophilic perfume ingredients, and even more preferably at least 7 different hydrophilic perfume ingredients. Most common perfume ingredients which are derived from natural sources are composed of a multitude of components. When each such material is used in the formulation of the preferred perfume compositions of the present invention, it is counted as one single ingredient, for the purpose of defining the invention.

(b). Low Odor Detection Threshold Perfume Ingredient

The odor detection threshold of an odorous material is the lowest vapor concentration of that material which can be olfactorily detected. The odor detection threshold and some odor detection threshold values are discussed in, e.g., "Standardized Human Olfactory Thresholds", M. Devos et al, IRL Press at Oxford University Press, 1990, and "Compilation of Odor and Taste Threshold Values Data", F. A. Fazzalari, editor, ASTM Data Series DS 48A, American Society for Testing and Materials, 1978, both of said publications being incorporated by reference. The use of small amounts of perfume ingredients that have low odor detection threshold values can improve perfume odor character, even though they are not as hydrophilic as perfume ingredients of group (a) which are given hereinabove. Perfume ingredients that do not belong to group (a) above, but have a significantly low detection threshold, useful in the composition of the present invention, are selected from the group consisting of ambrox, bacdanol, benzyl salicylate, butyl anthranilate, cetalox, damascenone, alpha-damascone, gamma-dodecalactone, ebanol, herbavert, cis-3-hexenyl salicylate, alpha-ionone, beta-ionone, alpha-isomethylionone, lilial, methyl nonyl ketone, gamma-undecalactone, undecylenic aldehyde, and mixtures thereof. These materials are preferably present at low levels in addition to the hydrophilic ingredients of group (a), typically less than about 20%, preferably less than about 15%, more preferably less than about 10%, by weight of the total perfume compositions of the present invention. However, only low levels are required to provide an effect.

There are also hydrophilic ingredients of group (a) that have a significantly low detection threshold, and are especially useful in the composition of the present invention.

Examples of these ingredients are allyl amyl glycolate, anethole, benzyl acetone, calone, cinnamic alcohol, coumarin, cyclogalbanate, Cyclal C, cymal, 4-decenal, dihydro isojasmonate, ethyl anthranilate, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl vanillin, eugenol, flor acetate, florhydral, fructose, frutene, heliotropin, keone, indole, iso cyclo citral, isoeugenol, lyral, methyl heptene carbonate, linalool, methyl anthranilate, methyl dihydrojasmonate, methyl isobutenyl tetrahydropyran, methyl beta naphthyl ketone, beta naphthol methyl ether, nerol, para-anisic aldehyde, para hydroxy phenyl butanone, phenyl acetaldehyde, vanillin, and mixtures thereof. Use of low odor detection threshold perfume ingredients minimizes the level of organic material that is released into the atmosphere.

(F) Low Molecular Weight Polyols

Low molecular weight polyols with relatively high boiling points, as compared to water, such as ethylene glycol, propylene glycol and/or glycerol are preferred optional ingredients for improving odor control performance of the composition of the present invention when cyclodextrin is present. Not to be bound by theory, it is believed that the incorporation of a small amount of low molecular weight glycols into the composition of the present invention enhances the formation of the cyclodextrin inclusion complexes as the fabric dries.

It is believed that the polyols' ability to remain on the fabric for a longer period of time than water, as the fabric dries allows it to form ternary complexes with the cyclodextrin and some malodorous molecules. The addition of the glycols is believed to fill up void space in the cyclodextrin cavity that is unable to be filled by some malodor molecules of relatively smaller sizes. Preferably the glycol used is glycerin, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol or mixtures thereof, more preferably ethylene glycol and propylene glycol. Cyclodextrins prepared by processes that result in a level of such polyols are highly desirable, since they can be used without removal of the polyols.

Some polyols, e.g., dipropylene glycol, are also useful to facilitate the solubilization of some perfume ingredients in the composition of the present invention.

Typically, glycol is added to the composition of the present invention at a level of from about 0.01% to about 3%, by weight of the composition, preferably from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of the composition. The preferred weight ratio of low molecular weight polyol to cyclodextrin is from about 2:1,000 to about 20:100, more preferably from about 3:1,000 to about 15:100, even more preferably from about 5:1,000 to about 10:100, and most preferably from about 1:100 to about 7:100.

(G) Cyclodextrin Preservative

Optionally, but if cyclodextrin is present, preferably, solubilized, water-soluble, antimicrobial preservative can be added to the composition of the present invention if the antimicrobial material C. is not sufficient to protect the cyclodextrin, or is not present, because cyclodextrin molecules are made up of varying numbers of glucose units which can make them a prime breeding ground for certain microorganisms, especially when in aqueous compositions. This drawback can lead to the problem of storage stability of cyclodextrin solutions for any significant length of time. Contamination by certain microorganisms with subsequent microbial growth can result in an unsightly and/or malodorous solution. Because microbial growth in cyclodextrin solutions is highly objectionable when it occurs, it is highly preferable to include a solubilized, water-soluble, antimicrobial preservative, which is effective for inhibiting and/or regulating microbial growth in order to increase storage stability of the preferably clear, aqueous odor-absorbing solution containing water-soluble cyclodextrin.

It is preferable to use a broad spectrum preservative, e.g., one that is effective on both bacteria (both gram positive and gram negative) and fungi. A limited spectrum preservative, e.g., one that is only effective on a single group of microorganisms, e.g., fungi, can be used in combination with a broad spectrum preservative or other limited spectrum preservatives with complimentary and/or supplementary activity. A mixture of broad spectrum preservatives can also be used. In some cases where a specific group of microbial contaminants is problematic (such as Gram negatives), aminocarboxylate chelators may be used alone or as potentiators in conjunction with other preservatives. These chelators which include, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can increase preservative effectiveness against Gram-negative bacteria, especially *Pseudomonas* species.

Antimicrobial preservatives useful in the present invention include biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate the growth of microorganisms. Suitable preservatives are disclosed in U.S. Pats. 5,534,165; 5,578,563; 5,663,134; 5,668,097; 5,670,475; and 5,714,137, Trinh et al. issued Jul. 9, 1996; Nov. 26, 1996; Sep. 2, 1997; Sep. 16, 1997; Sep. 23, 1997; and Feb. 3, 1998 respectively, all of said patents being incorporated hereinbefore by reference. Preferred antimicrobial preservatives are those that are water-soluble and are effective at low levels because the organic preservatives can form inclusion complexes with the cyclodextrin molecules and

compete with the malodorous molecules for the cyclodextrin cavities, thus rendering the cyclodextrins ineffective as odor controlling actives. Water-soluble preservatives useful in the present invention are those that have a solubility in water of at least about 0.3 g per 100 ml of water, i.e., greater than about 0.3% at room temperature, preferably greater than about 0.5% at room temperature. These types of preservatives have a lower affinity to the cyclodextrin cavity, at least in the aqueous phase, and are therefore more available to provide antimicrobial activity. Preservatives with a water-solubility of less than about 0.3% and a molecular structure that readily fits into the cyclodextrin cavity, have a greater tendency to form inclusion complexes with the cyclodextrin molecules, thus rendering the preservative less effective to control microbes in the cyclodextrin solution.

The water-soluble antimicrobial preservative in the present invention is included at an effective amount. The term "effective amount" as herein defined means a level sufficient to prevent spoilage, or prevent growth of inadvertently added microorganisms, for a specific period of time. In other words, the preservative is not being used to kill microorganisms on the surface onto which the composition is deposited in order to eliminate odors produced by microorganisms. Instead, it is preferably being used to prevent spoilage of the cyclodextrin solution in order to increase the shelf-life of the composition. Preferred levels of preservative are from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the usage composition.

In order to reserve most of the cyclodextrins for odor control, the cyclodextrin to preservative molar ratio should be greater than about 5:1, preferably greater than about 10:1, more preferably greater than about 50:1, even more preferably greater than about 100:1.

The preservative can be any organic preservative material which will not cause damage to fabric appearance, e.g., discoloration, coloration, bleaching. Preferred water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, quaternary ammonium compounds, dehydroacetic acid, phenyl and phenolic compounds, and mixtures thereof.

The preservatives of the present invention can be used in mixtures in order to control a broad range of microorganisms.

Bacteriostatic effects can sometimes be obtained for aqueous compositions by adjusting the composition pH to an acid pH, e.g., less than about pH 4, preferably less than about pH 3, or a basic pH, e.g., greater than about 10, preferably greater than about 11. Low pH for microbial control is not a preferred approach in the present invention because the low pH can cause chemical degradation of the cyclodextrins. High pH for

microbial control is also not preferred because at high pH's, e.g., greater than about 10, preferably greater than about 11, the cyclodextrins can be ionized and their ability to complex with organic materials is reduced. Therefore, aqueous compositions of the present invention should have a pH of from about 3 to about 10, preferably from about 4 to about 8, more preferably from about 4.5 to about 6. The pH is typically adjusted with inorganic molecules to minimize complexation with cyclodextrin.

(4). Antimicrobial Active

Optionally, the wrinkle control composition of the present invention comprise an effective amount, to kill, or reduce the growth of microbes, of antimicrobial active; preferably from about 0.001% to about 2%, more preferably from about 0.002% to about 1%, even more preferably from about 0.003% to about 0.3%, by weight of the usage composition. The effective antimicrobial active can function as disinfectants/sanitizers, and is useful in providing protection against organisms that become attached to the fabrics.

Given below are nonlimiting examples of antimicrobial actives which are useful in the present invention:

Pyrithiones, especially the zinc complex (ZPT); Octopirox; Parabens, including Methylparaben, Propylparaben, Butylparaben, Ethylparaben, Isopropylparaben, Isobutylparaben, Benzylparaben, Sodium Methylparaben, and Sodium Propylparaben; DMDM Hydantoin (Glydant); Methylchloroisothiazolinone/methylisothiazolinone (Kathon CG); Sodium Sulfite; Sodium Bisulfite; Imidazolidinyl Urea; Diazolidinyl Urea (Germall 2); Sorbic Acid/Potassium Sorbate; Dehydroacetic Acid/Sodium Dehydroacetate; Benzyl Alcohol; Sodium Borate; 2-Bromo-2-nitropropane-1,3-diol (Bronopol); Formalin; Iodopropynyl Butylcarbamate; Boric Acid; Chloroacetamide; Methenamine; Methylidibromo Glutaronitrile; Glutaraldehyde; Hexamidine Isethionate; 5-bromo-5-nitro-1,3-dioxane; Phenethyl Alcohol; o-Phenylphenol/sodium o-phenylphenol; Sodium Hydroxymethylglycinate; Polymethoxy Bicyclic Oxazolidine; Dimethoxane; Thimersol; Dichlorobenzyl alcohol; Captan; Chlorphenenesin; Dichlorophene; Chlorbutanol; Phenoxyethanol; Phenoxyisopropanol; Halogenated Diphenyl Ethers; 2,4,4'-trichloro-2'-hydroxy-diphenyl ether (Triclosan); 2,2'-dihydroxy-5,5'-dibromo-diphenyl ether;

Phenolic Compounds - (including phenol and its homologs, mono- and poly-alkyl and aromatic halophenols, resorcinol and its derivatives, bisphenolic compounds and halogenated salicylanilides); Phenol and its Homologs including Phenol, 2 Methyl Phenol, 3 Methyl Phenol, 4 Methyl Phenol, 4 Ethyl Phenol, 2,4-Dimethyl Phenol, 2,5-Dimethyl Phenol, 3,4-Dimethyl Phenol, 2,6-Dimethyl Phenol, 4-n-Propyl Phenol, 4-n-

Butyl Phenol, 4-n-Amyl Phenol, 4-tert-Amyl Phenol, 4-n-Hexyl Phenol, and 4-n-Heptyl Phenol; Mono- and Poly-Alkyl and Aromatic Halophenols including p-Chlorophenol, Methyl p-Chlorophenol, Ethyl p-Chlorophenol, n-Propyl p-Chlorophenol, n-Butyl p-Chlorophenol, n-Amyl p-Chlorophenol, sec-Amyl p-Chlorophenol, n-Hexyl p-Chlorophenol, Cyclohexyl p-Chlorophenol, n-Heptyl p-Chlorophenol, n-Octyl p-Chlorophenol, o-Chlorophenol, Methyl o-Chlorophenol, Ethyl o-Chlorophenol, n-Propyl o-Chlorophenol, n-Butyl o-Chlorophenol, n-Amyl o-Chlorophenol, tert-Amyl o-Chlorophenol, n-Hexyl o-Chlorophenol, n-Heptyl o-Chlorophenol, o-Benzyl p-Chlorophenol, o-benzyl-m-methyl p-Chlorophenol, o-Benzyl-m, m-dimethyl p-Chlorophenol, o-Phenylethyl p-Chlorophenol, o-Phenylethyl-m-methyl p-Chlorophenol, 3-Methyl p-Chlorophenol, 3,5-Dimethyl p-Chlorophenol, 6-Ethyl-3-methyl p-Chlorophenol, 6-n-Propyl-3-methyl p-Chlorophenol, 6-iso-Propyl-3-methyl p-Chlorophenol, 2-Ethyl-3,5-dimethyl p-Chlorophenol, 6-sec-Butyl-3-methyl p-Chlorophenol, 2-iso-Propyl-3,5-dimethyl p-Chlorophenol, 6-Diethylmethyl-3-methyl p-Chlorophenol, 6-iso-Propyl-2-ethyl-3-methyl p-Chlorophenol, 2-sec-Amyl-3,5-dimethyl p-Chlorophenol, 2-Diethylmethyl-3,5-dimethyl p-Chlorophenol, 6-sec-Octyl-3-methyl p-Chlorophenol, p-Chloro-m-cresol, p-Bromophenol, Methyl p-Bromophenol, Ethyl p-Bromophenol, n-Propyl p-Bromophenol, n-Butyl p-Bromophenol, n-Amyl p-Bromophenol, sec-Amyl p-Bromophenol, n-Hexyl p-Bromophenol, cyclohexyl p-Bromophenol, o-Bromophenol, tert-Amyl o-Bromophenol, n-Hexyl o-Bromophenol, n-Propyl-m,m-Dimethyl o-Bromophenol, 2-Phenyl Phenol, 4-Chloro-2-methyl phenol,

4-Chloro-3-methyl phenol, 4-Chloro-3,5-dimethyl phenol, 2,4-dichloro-3,5-dimethylphenol, 3,4,5,6-terabromo-2-methylphenol, 5-methyl-2-pentylphenol, 4-isopropyl-3-methylphenol, para-chloro-meta-xlenol (PCMX), 5-Chloro-2-hydroxydiphenylmethane; Resorcinol and its Derivatives including Resorcinol, Methyl Resorcinol, Ethyl Resorcinol, n-Propyl Resorcinol, n-Butyl Resorcinol, n-Amyl Resorcinol, n-Hexyl Resorcinol, n-Heptyl Resorcinol, n-Octyl Resorcinol, n-Nonyl Resorcinol, Phenyl Resorcinol, Benzyl Resorcinol, Phenylethyl Resorcinol, Phenylpropyl Resorcinol, p-Chlorobenzyl Resorcinol, 5-Chloro 2,4-Dihydroxydiphenyl Methane, 4'-Chloro 2,4-Dihydroxydiphenyl Methane, 5-Bromo 2,4-Dihydroxydiphenyl Methane, and 4' -Bromo 2,4-Dihydroxydiphenyl Methane; Bisphenolic Compounds including 2,2'-methylene bis (4-chlorophenol), 2,2'-methylene bis (3,4,6-trichlorophenol), 2,2'-methylene bis (4-chloro-6-bromophenol), bis (2-hydroxy-3,5-dichlorophenyl) sulphide, and bis (2-hydroxy-5-chlorobenzyl)sulphide; Benzoic Esters including p-Hydroxybenzoic Acid, Methyl p-Hydroxybenzoic Acid, Ethyl p-

Hydroxybenzoic Acid, Propyl p-Hydroxybenzoic Acid, and Butyl p-Hydroxybenzoic Acid.

Another class of antibacterial agents, which are useful in the present invention, are the so-called "natural" antibacterial actives, referred to as natural essential oils. These actives derive their names from their natural occurrence in plants. Typical natural essential oil antibacterial actives include oils of anise, lemon, orange, rosemary, wintergreen, thyme, lavender, cloves, hops, tea tree, citronella, wheat, barley, lemongrass, cedar leaf, cedarwood, cinnamon, fleagrass, geranium, sandalwood, violet, cranberry, eucalyptus, vervain, peppermint, gum benzoin, *Hydastis carradensis*, *Berberidaceae*, *daceae*, *Ratanhiae* and *Curcuma longa*. Also included in this class of natural essential oils are the key chemical components of the plant oils which have been found to provide the antimicrobial benefit. These chemicals include, but are not limited to anethol, catechole, camphene, thymol, eugenol, eucalyptol, ferulic acid, farnesol, hinokitiol, tropolone, limonene, menthol, methyl salicylate, salicylic acid, thymol, terpineol, verbenone, berberine, ratanhiae extract, caryophellene oxide, citronellic acid, curcumin, nerolidol, geraniol and benzoic acid.

Additional active agents are antibacterial metal salts. This class generally includes salts of metals in groups 3b-7b, 8 and 3a-5a. Specifically are the salts of aluminum, zirconium, zinc, silver, gold, copper, lanthanum, tin, mercury, bismuth, selenium, strontium, scandium, yttrium, cerium, praseodymium, neodymium, promethum, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and mixtures thereof.

Preferred antimicrobial agents for use herein are the broad spectrum actives selected from the group consisting of Triclosan, phenoxyisopropanol, phenoxyethanol, PCMX, natural essential oils and their key ingredients, and mixtures thereof. The most preferred antimicrobial active for use in the present invention is Triclosan.

Quaternary Compounds. A wide range of quaternary compounds can also be used as antimicrobial actives, in conjunction with the preferred surfactants, for compositions of the present invention. Non-limiting examples of useful quaternary compounds include: (1) benzalkonium chlorides and/or substituted benzalkonium chlorides such as commercially available Barquat® (available from Lonza), Maquat® (available from Mason), Variquat® (available from Witco/Sherex), and Hyamine® (available from Lonza); (2) di(C₆-C₁₄)alkyl di-short chain (C₁₋₄ alkyl and/or hydroxyalkyl) quaternary such as Bardac® products of Lonza. These quaternary compounds contain two relatively short chains, e.g., C₁₋₄ alkyl and/or hydroxy alkyl groups and two C₆₋₁₂, preferably C₆₋₁₀, and more preferably C₈, alkyl groups, (3) N-(3-

chloroallyl) hexaminium chlorides such as Dowicide® and Dowicil® available from Dow; (4) benzethonium chloride such as Hyamine® 1622 from Rohm & Haas; (5) methylbenzethonium chloride represented by Hyamine® 10X supplied by Rohm & Haas, (6) cetylpyridinium chloride such as Cepacol chloride available from Merrell Labs. Examples of the preferred dialkyl quaternary compounds are di(C8-C12)dialkyl dimethyl ammonium chloride, such as didecyldimethylammonium chloride (Bardac 22), and dioctyldimethylammonium chloride (Bardac 2050). Typical concentrations for biocidal effectiveness of these quaternary compounds range from about 0.001% to about 0.8%, preferably from about 0.005% to about 0.3%, more preferably from about 0.01% to 0.2%, by weight of the usage composition. The corresponding concentrations for the concentrated compositions are from about 0.003% to about 2%, preferably from about 0.006% to about 1.2%, and more preferably from about 0.1% to about 0.8% by weight of the concentrated compositions.

When cyclodextrin is present, the solubilized, water-soluble antimicrobial active is useful in providing protection against organisms that become attached to the treated fabrics. The antimicrobial should be cyclodextrin-compatible, e.g., not substantially forming complexes with the cyclodextrin in the odor absorbing composition when cyclodextrin is present. The free, uncomplexed antimicrobial, e.g., antibacterial, active provides an optimum antibacterial performance.

Sanitization of fabrics can be achieved by the compositions of the present invention containing, antimicrobial materials, e.g., antibacterial halogenated compounds, quaternary compounds, and phenolic compounds.

Biguanides. Some of the more robust cyclodextrin-compatible antimicrobial halogenated compounds which can function as disinfectants/sanitizers as well as finish product preservatives (vide infra), and are useful in the compositions of the present invention include 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with hydrochloric, acetic and gluconic acids. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorhexidine is used as a sanitizer in the present invention it is typically present at a level of from about 0.001% to about 0.4%, preferably from about 0.002% to about 0.3%, and more preferably from about 0.05% to about 0.2%, by weight of the usage composition. In some cases, a level of from about 1% to about 2% may be needed for virucidal activity.

Other useful biguanide compounds include Cosmoci® CQ®, Vantocil® IB, including poly (hexamethylene biguanide) hydrochloride. Other useful cationic antimicrobial agents include the bis-biguanide alkanes. Usable water soluble salts of the

above are chlorides, bromides, sulfates, alkyl sulfonates such as methyl sulfonate and ethyl sulfonate, phenylsulfonates such as p-methylphenyl sulfonates, nitrates, acetates, gluconates, and the like.

Examples of suitable bis biguanide compounds are chlorhexidine; 1,6-bis-(2-ethylhexylbiguanidohexane)dihydrochloride; 1,6-di-(N₁,N₁'-phenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di-(N₁,N₁'-phenyl-N₁,N₁'-methyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-2,6-dichlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di[N₁,N₁'-.beta.-(p-methoxyphenyl) diguanido-N₅,N₅']-hexane dihydrochloride; 1,6-di(N₁,N₁'-.alpha.-methyl-.beta.-phenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-p-nitrophenyldiguanido-N₅,N₅')-hexane dihydrochloride; omega.:omega'-di-(N₁,N₁'-phenyldiguanido-N₅,N₅')-di-n-propylether dihydrochloride; omega:omega'-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅')-di-n-propylether tetrahydrochloride; 1,6-di(N₁,N₁'-2,4-dichlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di(N₁,N₁'-p-methylphenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-2,4,5-trichlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di[N₁,N₁'-.alpha.-(p-chlorophenyl) ethyldiguanido-N₅,N₅'] hexane dihydrochloride; omega.:omega'-di(N₁, N₁'-p-chlorophenyldiguanido-N₅,N₅')-m-xylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane dihydrochloride; 1,10-di(N₁,N₁'-phenyldiguanido-N₅,N₅')-decane tetrahydrochloride; 1,12-di(N₁,N₁'-phenyldiguanido-N₅,N₅') dodecane tetrahydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') hexane dihydrochloride; 1,6-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; ethylene bis (1-tolyl biguanide); ethylene bis (p-tolyl biguanide); ethylene bis(3,5-dimethylphenyl biguanide); ethylene bis(p-tert-amyphenyl biguanide); ethylene bis(nonylphenyl biguanide); ethylene bis (phenyl biguanide); ethylene bis (N-butylphenyl biguanide); ethylene bis (2,5-diethoxyphenyl biguanide); ethylene bis(2,4-dimethylphenyl biguanide); ethylene bis(o-diphenylbiguanide); ethylene bis(mixed amyl naphthyl biguanide); N-butyl ethylene bis(phenylbiguanide); trimethylene bis(o-tolyl biguanide); N-butyl trimethylene bis(phenyl biguanide); and the corresponding pharmaceutically acceptable salts of all of the above such as the acetates; gluconates; hydrochlorides; hydrobromides; citrates; bisulfites; fluorides; polymaleates; N-coconutalkylsarcosinates; phosphites; hypophosphites; perfluorooctanoates; silicates; sorbates; salicylates; maleates; tartrates; fumarates; ethylenediaminetetraacetates; iminodiacetates; cinnamates; thiocyanates; arginates; pyromellitates; tetracarboxybutyrates; benzoates; glutarates; monofluorophosphates; and

perfluoropropionates, and mixtures thereof. Preferred antimicrobials from this group are 1,6-di-(N₁,N₁'-phenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-2,6-dichlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-2,4-dichlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di[N₁,N₁'-.alpha.-(p-chlorophenyl) ethyldiguanido-N₅,N₅'] hexane dihydrochloride; omega..omega.'di(N₁, N₁'-p-chlorophenyldiguanido-N₅,N₅')m-xylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane dihydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') hexane dihydrochloride; 1,6-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; and mixtures thereof; more preferably, 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-2,6-dichlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-2,4-dichlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di[N₁,N₁'-.alpha.-(p-chlorophenyl) ethyldiguanido-N₅,N₅'] hexane dihydrochloride; omega..omega.'di(N₁, N₁'-p-chlorophenyldiguanido-N₅,N₅')m-xylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane dihydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') hexane dihydrochloride; 1,6-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; and mixtures thereof. As stated hereinbefore, the bis biguanide of choice is chlorhexidine its salts, e.g., digluconate, dihydrochloride, diacetate, and mixtures thereof.

The surfactants, when added to the antimicrobials tend to provide improved antimicrobial action. This is especially true for the siloxane surfactants, and especially when the siloxane surfactants are combined with the chlorhexidine antimicrobial actives.

(5). Optional Aminocarboxylate Chelators

Chelators, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylene-diaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can optionally be used to increase antimicrobial and preservative effectiveness against Gram-negative bacteria, especially Pseudomonas species. Although sensitivity to EDTA and other aminocarboxylate chelators is mainly a characteristic of Pseudomonas species, other bacterial species highly susceptible to chelators include Achromobacter, Alcaligenes, Azotobacter, Escherichia, Salmonella, Spirillum, and Vibrio. Other groups of organisms also show increased sensitivities to these chelators, including fungi and yeasts. Furthermore, aminocarboxylate chelators can help, e.g., maintaining product clarity, protecting fragrance and perfume components, and preventing rancidity and off odors.

Although these aminocarboxylate chelators may not be potent biocides in their own right, they function as potentiators for improving the performance of other antimicrobials/preservatives in the compositions of the present invention. Aminocarboxylate chelators can potentiate the performance of many of the cationic, anionic, and nonionic antimicrobials/preservatives, phenolic compounds, and isothiazolinones, that are used as antimicrobials/preservatives in the composition of the present invention. Nonlimiting examples of cationic antimicrobials/preservatives potentiated by aminocarboxylate chelators in solutions are chlorhexidine salts (including digluconate, diacetate, and dihydrochloride salts), and Quaternium-15, also known as Dowicil 200, Dowicide Q, Preventol D1, benzalkonium chloride, cetrimonium, myristalkonium chloride, cetylpyridinium chloride, lauryl pyridinium chloride, and the like. Nonlimiting examples of useful anionic antimicrobials/preservatives which are enhanced by aminocarboxylate chelators are sorbic acid and potassium sorbate. Nonlimiting examples of useful nonionic antimicrobials/preservatives which are potentiated by aminocarboxylate chelators are DMDM hydantoin, phenethyl alcohol, monolaurin, imidazolidinyl urea, and Bronopol (2-bromo-2-nitropropane-1,3-diol).

Examples of useful phenolic antimicrobials/preservatives potentiated by these chelators are chloroxylenol, phenol, tert-butyl hydroxyanisole, salicylic acid, resorcinol, and sodium o-phenyl phenate. Nonlimiting examples of isothiazolinone antimicrobials/preservatives which are enhanced by aminocarboxylate chelators are Kathon, Proxel and Promexal.

The optional chelators are present in the compositions of this invention at levels of, typically, from about 0.01% to about 0.3%, more preferably from about 0.02% to about 0.1%, most preferably from about 0.02% to about 0.05% by weight of the usage compositions to provide antimicrobial efficacy in this invention.

Free, uncomplexed aminocarboxylate chelators are required to potentiate the efficacy of the antimicrobials. Thus, when excess alkaline earth (especially calcium and magnesium) and transitional metals (iron, manganese, copper, and others) are present, free chelators are not available and antimicrobial potentiation is not observed. In the case where significant water hardness or transitional metals are available or where product esthetics require a specified chelator level, higher levels may be required to allow for the availability of free, uncomplexed aminocarboxylate chelators to function as antimicrobial/preservative potentiators.

CARRIER

The preferred carrier of the present invention is water. The water which is used can be distilled, deionized, or tap water. Water is the main liquid carrier due to its low

cost, availability, safety, and environmental compatibility. Aqueous solutions are preferred for wrinkle control and odor control.

Water is very useful for fabric wrinkle removal or reduction. Not to be bound by theory, it is believed that water breaks many intrafiber and interfiber hydrogen bonds that keep the fabric in a wrinkle state. It also swells, lubricates and relaxes the fibers to help the wrinkle removal process.

Water also serves as the liquid carrier for the cyclodextrins, and facilitates the complexation reaction between the cyclodextrin molecules and any malodorous molecules that are on the fabric when it is treated. The dilute aqueous solution also provides the maximum separation of cyclodextrin molecules on the fabric and thereby maximizes the chance that an odor molecule will interact with a cyclodextrin molecule. It has recently also been discovered that water has an unexpected odor controlling effect of its own. It has been discovered that the intensity of the odor generated by some polar, low molecular weight organic amines, acids, and mercaptans is reduced when the odor-contaminated fabrics are treated with an aqueous solution. Not to be bound by theory, it is believed that water solubilizes and depresses the vapor pressure of these polar, low molecular weight organic molecules, thus reducing their odor intensity.

The level of liquid carrier in the compositions of the present invention is typically greater than about 80%, preferably greater than about 90%, more preferably greater than about 95%, by weight of the composition. When a concentrated composition is used, the level of liquid carrier is typically from about 50% to about 98%, by weight of the composition, preferably from about 60% to about 97%, more preferably from about 70% to about 95%, by weight of the composition.

Optionally, in addition to water, the carrier can contain a low molecular weight organic solvent that is highly soluble in water, e.g., ethanol, propanol, isopropanol, and the like, and mixtures thereof. Low molecular weight alcohols can help the treated fabric to dry faster. The optional solvent is also useful in the solubilization of some shape retention polymers described hereinbefore. The optional water soluble low molecular weight solvent can be used at a level of up to about 50%, typically from about 1% to about 20%, preferably from about 2% to about 15%, more preferably from about 5% to about 10%, by weight of the total composition. Factors that need to consider when a high level of solvent is used in the composition are odor, flammability, and environment impact.

OTHER OPTIONAL INGREDIENTS

The composition of the present invention can optionally contain adjunct odor-controlling materials, chelating agents, antistatic agents, insect and moth repelling agents, colorants, especially bluing agents, antioxidants, and mixtures thereof in addition to the cyclic silicone molecules. The total level of optional ingredients is low, preferably less than about 5%, more preferably less than about 3%, and even more preferably less than about 2%, by weight of the usage composition. These optional ingredients exclude the other ingredients specifically mentioned hereinbefore. Incorporating adjunct odor-controlling materials can enhance the capacity of the cyclodextrin to control odors as well as broaden the range of odor types and molecule sizes which can be controlled. Such materials include, for example, metallic salts, water-soluble cationic and anionic polymers, zeolites, water-soluble bicarbonate salts, and mixtures thereof.

(1) Water-Soluble Polyionic Polymers

Some water-soluble polyionic polymers, e.g., water-soluble cationic polymer and water-soluble anionic polymers can be used in the composition of the present invention to provide additional odor control benefits.

a. Cationic polymers, e.g., polyamines

Water-soluble cationic polymers, e.g., those containing amino functionalities, amido functionalities, and mixtures thereof, are useful in the present invention to control certain acid-type odors.

b. Anionic polymers, e.g., polyacrylic acid

Water-soluble anionic polymers, e.g., polyacrylic acids and their water-soluble salts are useful in the present invention to control certain amine-type odors. Preferred polyacrylic acids and their alkali metal salts have an average molecular weight of less than about 20,000, more preferably less than 5,000,000, preferably less than 10,000, more preferably from about 500 to about 5,000. Polymers containing sulfonic acid groups, phosphoric acid groups, phosphonic acid groups, and their water-soluble salts, and mixtures thereof, and mixtures with carboxylic acid and carboxylate groups, are also suitable.

Water-soluble polymers containing both cationic and anionic functionalities are also suitable. Examples of these polymers are given in U.S. Pat. 4,909,986, issued March 20, 1990 to N. Kobayashi and A. Kawazoe, incorporated herein by reference. Another example of water-soluble polymers containing both cationic and anionic functionalities is a copolymer of dimethyldiallyl ammonium chloride and acrylic acid, commercially available under the trade name Merquat 280® from Calgon.

When a water-soluble polymer is used it is typically present at a level of from about 0.001% to about 3%, preferably from about 0.005% to about 2%, more preferably

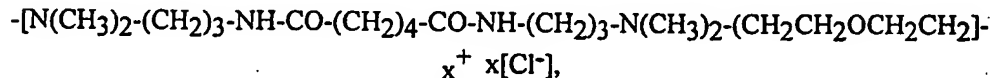
from about 0.01% to about 1%, and even more preferably from about 0.05% to about 0.5%, by weight of the usage composition.

(4). Antistatic Agents

The composition of the present invention can optionally contain an effective amount of antistatic agent to provide the treated clothes with in-wear static. Preferred antistatic agents are those that are water soluble in at least an effective amount, such that the composition remains a clear solution. Examples of these antistatic agents are monoalkyl cationic quaternary ammonium compounds, e.g., mono(C₁₀-C₁₄ alkyl)trimethyl ammonium halide, such as monolauryl trimethyl ammonium chloride, hydroxycetyl hydroxyethyl dimethyl ammonium chloride, available under the trade name Dehyquart E[®] from Henkel, and ethyl bis(polyethoxy ethanol) alkylammonium ethylsulfate, available under the trade name Variquat 66[®] from Witco Corp., polyethylene glycols, polymeric quaternary ammonium salts, such as polymers conforming to the general formula:



available under the trade name Mirapol A-15[®] from Rhône-Poulenc, and



available under the trade name Mirapol AD-1[®] from Rhône-Poulenc, quaternized polyethyleneimines, vinylpyrrolidone/methacrylamidopropyltrimethylammonium chloride copolymer, available under the trade name Gafquat HS-100[®] from GAF; triethonium hydrolyzed collagen ethosulfate, available under the trade name Quat-Pro E[®] from Maybrook; neutralized sulfonated polystyrene, available, e.g., under the trade name Versa TL-130[®] from Alco Chemical, neutralized sulfonated styrene/maleic anhydride copolymers, available, e.g., under the trade name Versa TL-4[®] from Alco Chemical; and mixtures thereof.

It is preferred that a no foaming, or low foaming, agent is used, to avoid foam formation during fabric treatment. It is also preferred that polyethoxylated agents such as polyethylene glycol or Variquat 66[®] are not used when alpha-cyclodextrin is used. The polyethoxylate groups have a strong affinity to, and readily complex with, alpha-cyclodextrin which in turn depletes the uncomplexed cyclodextrin available for odor control.

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When an antistatic agent is used it is typically present at a level of from about 0.05% to about 10%, preferably from about 0.1% to about 5%, more preferably from about 0.3% to about 3%, by weight of the usage composition.

(5). Insect and/or Moth Repelling Agent

The composition of the present invention can optionally contain an effective amount of insect and/or moth repelling agents. Typical insect and moth repelling agents are pheromones, such as anti-aggregation pheromones, and other natural and/or synthetic ingredients. Preferred insect and moth repellent agents useful in the composition of the present invention are perfume ingredients, such as citronellol, citronellal, citral, linalool, cedar extract, geranium oil, sandalwood oil, 2-(diethylphenoxy)ethanol, 1-dodecene, etc. Other examples of insect and/or moth repellents useful in the composition of the present invention are disclosed in U.S. Pat. Nos. 4,449,987, 4,693,890, 4,696,676, 4,933,371, 5,030,660, 5,196,200, and in "Semio Activity of Flavor and Fragrance Molecules on Various Insect Species", B.D. Mookherjee et al., published in Bioactive Volatile Compounds from Plants, ASC Symposium Series 525, R. Teranishi, R.G. Buttery, and H. Sugisawa, 1993, pp. 35-48, all of said patents and publications being incorporated herein by reference. When an insect and/or moth repellent is used it is typically present at a level of from about 0.005% to about 3%, by weight of the usage composition.

(6). Colorant

Colorants and dyes, especially bluing agents, can be optionally added to the wrinkle control compositions for visual appeal and performance impression. When colorants are used, they are used at extremely low levels to avoid fabric staining. Preferred colorants for use in the present compositions are highly water-soluble dyes, e.g., Liquitint® dyes available from Milliken Chemical Co. Non-limiting examples of suitable dyes are, Liquitint Blue HP®, Liquitint Blue 65®, Liquitint Patent Blue®, Liquitint Royal Blue®, Liquitint Experimental Yellow 8949-43®, Liquitint Green HMC®, Liquitint Yellow II®, and mixtures thereof, preferably Liquitint Blue HP®, Liquitint Blue 65®, Liquitint Patent Blue®, Liquitint Royal Blue®, Liquitint Experimental Yellow 8949-43®, and mixtures thereof.

(7). Optional Anti-Clogging Agent

Optional anti-clogging agent which enhances the wetting and anti-clogging properties of the composition, especially when starch is present, is chosen from the group of polymeric glycols of alkanes and olefins having from 2 to about 6, preferably 2 carbon atoms. The anti-clogging agent inhibits the formation of "plugs" in the spray nozzle. An example of the preferred anti-clogging agent is polyethylene glycol having an average molecular weight of from about 800 to about 12,000, more preferably from about 1,400

to about 8,000. When used, the anti-clogging agent is present at a level of from about 0.01% to about 1%, preferably from about 0.05% to about 0.5%, more preferably, from about 0.1% to about 0.3% by weight of the usage composition.

(8) Mixtures thereof

II. ARTICLE OF MANUFACTURE

The composition of the present invention can also be used in an article of manufacture comprising said composition plus a spray dispenser. When the commercial embodiment of the article of manufacture is used, it is optional, but preferable, to include the preservative. Therefore, the most basic article of manufacture comprises a wrinkle control agent, a carrier, and a spray dispenser.

SPRAY DISPENSER

The article of manufacture herein comprises a spray dispenser. The fabric wrinkle control composition is placed into a spray dispenser in order to be distributed onto the fabric. Said spray dispenser for producing a spray of liquid droplets can be any of the manually activated means as is known in the art, e.g. trigger-type, pump-type, non-aerosol self-pressurized, and aerosol-type spray means, for treating the wrinkle control composition to small fabric surface areas and/or a small number of garments, as well as non-manually operated, powered sprayers for conveniently treating the wrinkle control composition to large fabric surface areas and/or a large number of garments. The spray dispenser herein does not normally include those that will substantially foam the clear, aqueous wrinkle control composition. It has been found that the performance is increased by providing smaller particle droplets. Desirably, the Sauter mean particle diameter is from about 10 μm to about 120 μm , more preferably, from about 20 μm to about 100 μm . Dewrinkling benefits are improved by providing small particles (droplets), as discussed hereinbefore, especially when the surfactant is present.

The spray dispenser can be an aerosol dispenser. Said aerosol dispenser comprises a container which can be constructed of any of the conventional materials employed in fabricating aerosol containers. The dispenser must be capable of withstanding internal pressure in the range of from about 20 to about 110 p.s.i.g., more preferably from about 20 to about 70 p.s.i.g. The one important requirement concerning the dispenser is that it be provided with a valve member which will permit the clear, aqueous dewrinkle composition contained in the dispenser to be dispensed in the form of a spray of very fine, or finely divided, particles or droplets. The aerosol dispenser utilizes a pressurized sealed container from which the clear, aqueous dewrinkle composition is dispensed through a special actuator/valve assembly under pressure. The aerosol dispenser is pressurized by incorporating therein a gaseous component generally

known as a propellant. Common aerosol propellants, e.g., gaseous hydrocarbons such as isobutane, and mixed halogenated hydrocarbons, can be used. Halogenated hydrocarbon propellants such as chlorofluoro hydrocarbons have been alleged to contribute to environmental problems, and are not preferred. When cyclodextrin is present hydrocarbon propellants are not preferred, because they can form complexes with the cyclodextrin molecules thereby reducing the availability of uncomplexed cyclodextrin molecules for odor absorption. Preferred propellants are compressed air, nitrogen, inert gases, carbon dioxide, etc. A more complete description of commercially available aerosol-spray dispensers appears in U.S. Pat. Nos.: 3,436,772, Stebbins, issued April 8, 1969; and 3,600,325, Kaufman et al., issued August 17, 1971; both of said references are incorporated herein by reference.

Preferably the spray dispenser can be a self-pressurized non-aerosol container having a convoluted liner and an elastomeric sleeve. Said self-pressurized dispenser comprises a liner/sleeve assembly containing a thin, flexible radially expandable convoluted plastic liner of from about 0.010 to about 0.020 inch thick, inside an essentially cylindrical elastomeric sleeve. The liner/sleeve is capable of holding a substantial quantity of wrinkle control composition product and of causing said product to be dispensed. A more complete description of self-pressurized spray dispensers can be found in U.S. Pat. Nos. 5,111,971, Winer, issued May 12, 1992, and 5,232,126, Winer, issued Aug. 3, 1993; both of said references are herein incorporated by reference. Another type of aerosol spray dispenser is one wherein a barrier separates the wrinkle control composition from the propellant (preferably compressed air or nitrogen), as disclosed in U.S. Pat. No. 4,260,110, issued April 7, 1981, and incorporated herein by reference. Such a dispenser is available from EP Spray Systems, East Hanover, New Jersey.

More preferably, the spray dispenser is a non-aerosol, manually activated, pump-spray dispenser. Said pump-spray dispenser comprises a container and a pump mechanism which securely screws or snaps onto the container. The container comprises a vessel for containing the aqueous wrinkle control composition to be dispensed.

The pump mechanism comprises a pump chamber of substantially fixed volume, having an opening at the inner end thereof. Within the pump chamber is located a pump stem having a piston on the end thereof disposed for reciprocal motion in the pump chamber. The pump stem has a passageway there through with a dispensing outlet at the outer end of the passageway and an axial inlet port located inwardly thereof.

The container and the pump mechanism can be constructed of any conventional material employed in fabricating pump-spray dispensers, including, but not limited to:

polyethylene; polypropylene; polyethyleneterephthalate; blends of polyethylene, vinyl acetate, and rubber elastomer. A preferred container is made of clear, e.g., polyethylene terephthalate. Other materials can include stainless steel. A more complete disclosure of commercially available dispensing devices appears in: U.S. Pat. Nos.: 4,895,279, Schultz, issued January 23, 1990; 4,735,347, Schultz et al., issued April 5, 1988; and 4,274,560, Carter, issued June 23, 1981; all of said references are herein incorporated by reference.

Most preferably, the spray dispenser is a manually activated trigger-spray dispenser. Said trigger-spray dispenser comprises a container and a trigger both of which can be constructed of any of the conventional material employed in fabricating trigger-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyacetal; polycarbonate; polyethyleneterephthalate; polyvinyl chloride; polystyrene; blends of polyethylene, vinyl acetate, and rubber elastomer. Other materials can include stainless steel and glass. A preferred container is made of clear, e.g. polyethylene terephthalate. The trigger-spray dispenser does not incorporate a propellant gas into the odor-absorbing composition, and preferably it does not include those that will foam the wrinkle control composition. The trigger-spray dispenser herein is typically one which acts upon a discrete amount of the wrinkle control composition itself, typically by means of a piston or a collapsing bellows that displaces the composition through a nozzle to create a spray of thin liquid. Said trigger-spray dispenser typically comprises a pump chamber having either a piston or bellows which is movable through a limited stroke response to the trigger for varying the volume of said pump chamber. This pump chamber or bellows chamber collects and holds the product for dispensing. The trigger spray dispenser typically has an outlet check valve for blocking communication and flow of fluid through the nozzle and is responsive to the pressure inside the chamber. For the piston type trigger sprayers, as the trigger is compressed, it acts on the fluid in the chamber and the spring, increasing the pressure on the fluid. For the bellows spray dispenser, as the bellows is compressed, the pressure increases on the fluid. The increase in fluid pressure in either trigger spray dispenser acts to open the top outlet check valve. The top valve allows the product to be forced through the swirl chamber and out the nozzle to form a discharge pattern. An adjustable nozzle cap can be used to vary the pattern of the fluid dispensed.

For the piston spray dispenser, as the trigger is released, the spring acts on the piston to return it to its original position. For the bellows spray dispenser, the bellows acts as the spring to return to its original position. This action causes a vacuum in the

chamber. The responding fluid acts to close the outlet valve while opening the inlet valve drawing product up to the chamber from the reservoir.

A more complete disclosure of commercially available dispensing devices appears in U.S. Pat. Nos. 4,082,223, Nozawa, issued Apr. 4, 1978; 4,161, 288, McKinney, issued Jul. 17, 1985; 4,434,917, Saito et al., issued Mar. 6, 1984; and 4,819,835, Tasaki, issued Apr. 11, 1989; 5,303,867, Peterson, issued Apr. 19, 1994; all of said references are incorporated herein by reference.

A broad array of trigger sprayers or finger pump sprayers are suitable for use with the compositions of this invention. These are readily available from suppliers such as Calmar, Inc., City of Industry, California; CSI (Continental Sprayers, Inc.), St. Peters, Missouri; Berry Plastics Corp., Evansville, Indiana, a distributor of Guala[®] sprayers; or Seaquest Dispensing, Cary, Illinois.

The preferred trigger sprayers are the blue inserted Guala[®] sprayer, available from Berry Plastics Corp., or the Calmar TS800-1A[®], TS1300[®], and TS-800-2[®], available from Calmar Inc., because of the fine uniform spray characteristics, spray volume, and pattern size. More preferred are sprayers with precompression features and finer spray characteristics and even distribution, such as Yoshino sprayers from Japan. Any suitable bottle or container can be used with the trigger sprayer, the preferred bottle is a 17 fl-oz. bottle (about 500 ml) of good ergonomics similar in shape to the Cinch[®] bottle. It can be made of any materials such as high density polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene terephthalate, glass, or any other material that forms bottles. Preferably, it is made of high density polyethylene or clear polyethylene terephthalate.

For smaller fluid ounce sizes (such as 1 to 8 ounces), a finger pump can be used with canister or cylindrical bottle. The preferred pump for this application is the cylindrical Euromist II[®] from Seaquest Dispensing. More preferred are those with precompression features.

The article of manufacture herein can also comprise a non-manually operated spray dispenser. By "non-manually operated" it is meant that the spray dispenser can be manually activated, but the force required to dispense the wrinkle control composition is provided by another, non-manual means. Non-manually operated sprayers include, but are not limited to, powered sprayers, air aspirated sprayers, liquid aspirated sprayers, electrostatic sprayers, and nebulizer sprayers. The wrinkle control composition is placed into a spray dispenser in order to be distributed onto the fabric.

Powered sprayers include self contained powered pumps that pressurize the aqueous dewrinkle composition and dispense it through a nozzle to produce a spray of

liquid droplets. Powered sprayers are attached directly or remotely through the use of piping/tubing to a reservoir (such as a bottle) to hold the aqueous wrinkle control composition. Powered sprayers may include, but are not limited to, centrifugal or positive displacement designs. It is preferred that the powered sprayer be powered by a portable DC electrical current from either disposable batteries (such as commercially available alkaline batteries) or rechargeable battery units (such as commercially available nickel cadmium battery units). Powered sprayers may also be powered by standard AC power supply available in most buildings. The discharge nozzle design can be varied to create specific spray characteristics (such as spray diameter and particle size). It is also possible to have multiple spray nozzles for different spray characteristics. The nozzle may or may not contain an adjustable nozzle shroud that would allow the spray characteristics to be altered.

Nonlimiting examples of commercially available powered sprayers are disclosed in U.S. Pat. Nos. 4,865,255, Luvisotto, issued Sep. 12, 1989 which is incorporated herein by reference. Preferred powered sprayers are readily available from suppliers such as Solo, Newport News, Virginia (e.g., Solo SpraystarTM rechargeable sprayer, listed as manual part #: US 460 395) and Multi-sprayer Systems, Minneapolis, Minnesota (e.g., model: Spray 1).

Air aspirated sprayers include the classification of sprayers generically known as "air brushes". A stream of pressurized air draws up the aqueous wrinkle control composition and dispenses it through a nozzle to create a spray of liquid. The wrinkle control composition can be supplied via separate piping/tubing or more commonly is contained in a jar to which the aspirating sprayer is attached.

Nonlimiting examples of commercially available air aspirated sprayers appears in U.S. Pat. Nos. 1,536,352, Murray, issued Apr. 22, 1924 and 4,221,339, Yoshikawa, issued Sep. 9, 1980; all of said references are incorporated herein by reference. Air aspirated sprayers are readily available from suppliers such as The Badger Air-Brush Co., Franklin Park, Illinois (e.g., model #: 155) and Wilton Air Brush Equipment, Woodridge, Illinois (e.g., stock #: 415-4000, 415-4001, 415-4100).

Liquid aspirated sprayers are typical of the variety in widespread use to spray garden chemicals. The aqueous dewrinkling composition is drawn into a fluid stream by means of suction created by a Venturi effect. The high turbulence serves to mix the aqueous wrinkle control composition with the fluid stream (typically water) in order to provide a uniform mixture/concentration. It is possible with this method of delivery to dispense the aqueous concentrated wrinkle control composition of the present invention and then dilute it to a selected concentration with the delivery stream.

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Liquid aspirated sprayers are readily available from suppliers such as Chapin Manufacturing Works, Batavia, New York (e.g., model #: 6006).

Electrostatic sprayers impart energy to the aqueous dewrinkling composition via a high electrical potential. This energy serves to atomize and charge the aqueous wrinkle control composition, creating a spray of fine, charged particles. As the charged particles are carried away from the sprayer, their common charge causes them to repel one another. This has two effects before the spray reaches the target. First, it expands the total spray mist. This is especially important when spraying to fairly distant, large areas. The second effect is maintenance of original particle size. Because the particles repel one another, they resist collecting together into large, heavier particles like uncharged particles do. This lessens gravity's influence, and increases the charged particle reaching the target. As the mass of negatively charged particles approach the target, they push electrons inside the target inwardly, leaving all the exposed surfaces of the target with a temporary positive charge. The resulting attraction between the particles and the target overrides the influences of gravity and inertia. As each particle deposits on the target, that spot on the target becomes neutralized and no longer attractive. Therefore, the next free particle is attracted to the spot immediately adjacent and the sequence continues until the entire surface of the target is covered. Hence, charged particles improve distribution and reduce drippage.

Nonlimiting examples of commercially available electrostatic sprayers appears in U.S. Pat. Nos. 5,222,664, Noakes, issued Jun. 29, 1993; 4,962,885, Coffee, issued Oct. 16, 1990; 2,695,002, Miller, issued Nov. 1954; 5,405,090, Greene, issued Apr. 11, 1995; 4,752,034, Kuhn, issued Jun. 21, 1988; 2,989,241, Badger, issued Jun. 1961; all of said patents are incorporated herein by reference. Electrostatic sprayers are readily available from suppliers such as Tae In Tech Co, South Korea and Spectrum, Houston, Texas.

Nebulizer sprayers impart energy to the aqueous dewrinkling composition via ultrasonic energy supplied via a transducer. This energy results in the aqueous wrinkle control composition to be atomized. Various types of nebulizers include, but are not limited to, heated, ultrasonic, gas, venturi, and refillable nebulizers.

Nonlimiting examples of commercially available nebulizer sprayers appears in U.S. Pat. Nos. 3,901,443, Mitsui, issued Aug. 26, 1975; 2,847,248, Schmitt, issued Aug. 1958; 5,511,726, Greenspan, issued Apr. 30, 1996; all of said patents are incorporated herein by reference. Nebulizer sprayers are readily available from suppliers such as A&D Engineering, Inc., Milpitas, California (e.g., model A&D Un-231 ultrasonic handy nebulizer) and Amici, Inc., Spring City, Pennsylvania (model: swirler nebulizer).

The preferred article of manufacture herein comprises a non-manually operated sprayer, such as a battery-powered sprayer, containing the aqueous wrinkle control composition. More preferably the article of manufacture comprises a combination of a non-manually operated sprayer and a separate container of the aqueous wrinkle control composition, to be added to the sprayer before use and/or to be separated for filling/refilling. The separate container can contain an usage composition, or a concentrated composition to be diluted before use, and/or to be used with a diluting sprayer, such as with a liquid aspirated sprayer, as described herein above.

Also, as described hereinbefore, the separate container should have structure that mates with the rest of the sprayer to ensure a solid fit without leakage, even after motion, impact, etc. and when handled by inexperienced consumers. The sprayer desirably can also have an attachment system that is safe and preferably designed to allow for the liquid container to be replaced by another container that is filled. E.g., the fluid reservoir can be replaced by a filled container. This can minimize problems with filling, including minimizing leakage, if the proper mating and sealing means are present on both the sprayer and the container. Desirably, the sprayer can contain a shroud to ensure proper alignment and/or to permit the use of thinner walls on the replacement container. This minimizes the amount of material to be recycled and/or discarded. The package sealing or mating system can be a threaded closure (sprayer) which replaces the existing closure on the filled and threaded container. A gasket is desirably added to provide additional seal security and minimize leakage. The gasket can be broken by action of the sprayer closure. These threaded sealing systems can be based on industry standards. However, it is highly desirable to use a threaded sealing system that has non-standard dimensions to ensure that the proper sprayer/bottle combination is always used. This helps prevent the use of fluids that are toxic, which could then be dispensed when the sprayer is used for its intended purpose.

An alternative sealing system can be based on one or more interlocking lugs and channels. Such systems are commonly referred to as "bayonet" systems. Such systems can be made in a variety of configurations, thus better ensuring that the proper replacement fluid is used. For convenience, the locking system can also be one that enables the provision of a "child-proof" cap on the refill bottle. This "lock-and-key" type of system thus provides highly desirable safety features. There are a variety of ways to design such lock and key sealing systems.

Care must be taken, however, to prevent the system from making the filling and sealing operation too difficult. If desired, the lock and key can be integral to the sealing mechanism. However, for the purpose of ensuring that the correct recharge or refill is

used, the interlocking pieces can be separate from the sealing system. E.g., the shroud and the container could be designed for compatibility. In this way, the unique design of the container alone could provide the requisite assurance that the proper recharge/refill is used.

Examples of threaded closures and bayonet systems can be found in U.S. Pat. 4,781,311, Nov. 1, 1988 (Angular Positioned Trigger Sprayer with Selective Snap-Screw Container Connection, Clorox), U.S. Pat. 5,560,505, Oct. 1, 1996 (Container and Stopper Assembly Locked Together by Relative Rotation and Use Thereof, Cebal SA), and U.S. Pat. 5,725,132, Mar. 10, 1998 (Dispenser with Snap-Fit Container Connection, Centico International). All of said patents are incorporated herein by reference.

III. METHOD OF USE

The wrinkle control composition, which optionally contains, e.g., surfactant, antimicrobial compound, etc., can be used by distributing, e.g., by placing, an effective amount of the aqueous solution onto the surface or article to be treated. Distribution can be achieved by using a spray device, a roller, a pad, etc., preferably a spray dispenser. For wrinkle control, an effective amount means an amount sufficient to remove or noticeably reduce the appearance of wrinkles on fabric. For odor control, an effective amount, as defined herein, means an amount sufficient to absorb odor to effect a noticeable reduction in the perceived odor, preferably to the point that it is not discernible, by the human sense of smell. Preferably, the amount of solution is not so much as to saturate or create a pool of liquid on said article or surface and so that when dry there is no visual deposit readily discernible.

Preferably, the present invention does not encompass distributing the composition onto non-fabric surfaces. However when there is cyclodextrin in the composition it can be used on other surfaces for odor control. However, care should be taken when treating such composition on shiny surfaces including, e.g., chrome, glass, smooth vinyl, leather, shiny plastic, shiny wood, etc., because spotting and filming can occur on such surfaces. However, when appearance is not important, the composition of the present invention containing cyclodextrin can be sprayed onto shiny surfaces to obtain odor control benefit. Although the cyclodextrin solution can be used on human skin, care should be taken, especially when an antimicrobial active is present in the composition.

The compositions and articles of the present invention which contain a fabric wrinkle control agent can be used to treat fabrics, garments, and the like to remove or reduce, undesirable wrinkles, in addition to the optional removal or reduction of undesirable odor on said objects.

An effective amount of the liquid composition of the present invention is preferably sprayed onto fabrics, particularly clothing. When the composition is sprayed onto fabric, an effective amount should be deposited onto the fabric, with the fabric becoming damp or totally saturated with the composition, typically from about 5% to about 150%, preferably from about 10% to about 100%, more preferably from about 20% to about 75%, by weight of the fabric. The amount of volatile silicone active typically sprayed onto the fabric is from about 0.001% to about 1%, preferably from about 0.01% to about 0.5%, more preferably from about 0.02% to about 0.2%, by weight of the fabric. Once an effective amount of the composition is sprayed onto the fabric the fabric is optionally, but preferably stretched. The fabric is typically stretched perpendicular to the wrinkle. The fabric can also be smoothed by hand after it has been sprayed. The smoothing movement works particularly well on areas of clothing that have an interface sewn into them, or on the hems of clothing. Once the fabric has been sprayed and optionally, but preferably, stretched, it is hung until dry.

The compositions of the present invention can also be used as ironing aids. An effective amount of the composition can be sprayed onto fabric and the fabric is ironed at the normal temperature at which it should be ironed. The fabric can either be sprayed with an effective amount of the composition, allowed to dry and then ironed, or sprayed and ironed immediately.

In a still further aspect of the invention, the composition can be sprayed onto fabrics by in an in-home de-wrinkling chamber containing the fabric to be dewrinkled and/or optionally deodorized, thereby providing ease of operation. Conventional personal as well as industrial deodorizing and/or de-wrinkling apparatuses are suitable for use herein. Traditionally, these apparatuses act by a steaming process which effects a relaxation of the fibers. Examples of home dewrinkling chambers include shower stalls. The spraying of the composition or compounds onto the fabrics can then occur within the chamber of the apparatus or before placing the fabrics into the chamber. Again, the spraying means should preferably be capable of providing droplets with a weight average diameter of from about 8 to about 100 μm , preferably from about 10 to about 50 μm . Preferably, the loading of moisture on fabrics made of natural and synthetic fibers is from about 5 to about 25%, more preferably from about 5 to about 10% by weight of the dried fabric. Other conventional steps that can be carried out in the dewrinkling apparatus can be applied such as heating and drying. Preferably, for optimum dewrinkling benefit, the temperature profile inside the chamber ranges from about 40°C to about 80°C, more preferably from about 50°C to about 70°C. The preferred length of the drying cycle is from about 15 to about 60 minutes, more preferably from about 20 to about 45 minutes.

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The steaming step in the dewrinkling apparatus may also be eliminated if the composition is maintained at a temperature range from about 22°C (about 72°F) to about 76°C (170°F) before spraying.

The present invention encompasses the method of spraying a mist of an effective amount of cyclodextrin solution onto fabric and/or fabric articles. Preferably, said fabric and/or fabric articles include, but are not limited to, clothes, curtains, drapes, upholstered furniture, carpeting, bed linens, bath linens, tablecloths, sleeping bags, tents, car interiors, etc.

The compositions herein are especially useful, when used to treat garments for extending the time before another wash cycle is needed. Such garments include uniforms and other garments which are normally treated in an industrial process, which can be dewrinkled and/or refreshed and the time between treatments extended.

The presence of the highly preferred surfactant promotes spreading of the solution and the highly preferred antimicrobial active provides improved odor control as well as antimicrobial action, by minimizing the formation of odors. Both the surfactant and the antimicrobial active provide improved performance and the mixture is especially good. When the compositions are applied in the form of the very small particles (droplets), as disclosed hereinbefore, additional benefits are found, since the distribution is even further improved and overall performance is improved.

All percentages, ratios, and parts herein, in the Specification, Examples, and Claims are by weight and are the normal approximations unless otherwise stated.

The following are non-limiting examples of the instant composition. The following compositions are prepared by mixing and dissolving the ingredients into clear or translucent solutions.

Examples I

<u>Examples</u> <u>Ingredients</u>	<u>Ia</u> <u>Wt%</u>	<u>Ib</u> <u>Wt%</u>	<u>Ic</u> <u>Wt%</u>	<u>Id</u> <u>Wt%</u>	<u>Ie</u> <u>Wt%</u>	<u>If</u> <u>Wt%</u>
D5 volatile silicone	0.5	0.5	0.5	0.35	1.0	1.0
Silwet L-7602	0.7	--	--	--	--	--
Silwet L-7622	--	0.5	--	0.7	--	0.8
Silwet L-7604	--	--	0.5	--	--	--
Silwet L-7210	--	--	--	0.5	--	--
Silwet L-7001	--	--	--	--	1.0	--
Silwet L-7600	--	--	--	--	--	0.4
Perfume	0.1	0.1	0.05	0.1	0.03	0.05
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

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Examples II

<u>Examples</u> <u>Ingredients</u>	<u>IIa</u> <u>Wt%</u>	<u>IIb</u> <u>Wt%</u>	<u>IIc</u> <u>Wt%</u>	<u>IId</u> <u>Wt%</u>	<u>IIe</u> <u>Wt%</u>	<u>II f</u> <u>Wt%</u>
Lithium bromide	3.0	--	2.0	1.0	2.5	--
Lithium lactate	--	3.0	--	--	--	2.0
D5 volatile silicone	0.5	--	--	0.25	--	--
Silicone emulsion A ⁽¹⁾	--	2.0	--	1.0	--	--
Silicone emulsion B ⁽²⁾	--	--	2.0	--	--	--
Silwet L-7210	0.5	--	--	--	0.1	--
Silwet L-7602	--	0.1	--	--	0.1	--
Silwet L-7622	--	--	0.1	0.4	--	--
Perfume	0.1	0.03	0.03	0.05	0.03	--
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

- (1) DC-2-5932 silicone microemulsion (25% active) from Dow Corning, with a particle size of about 24 nm, a cationic surfactant system, and a silicone with an internal phase viscosity of about 1,200 cps.
- (2) DC-1550 silicone microemulsion (25% active) from Dow Corning, with a particle size of about 50 nm, an anionic/nonionic surfactant system, and a silicone with an internal phase viscosity of about 100,000 cps.

Examples III

<u>Examples</u> <u>Ingredients</u>	<u>IIIa</u> <u>Wt%</u>	<u>IIIb</u> <u>Wt%</u>	<u>IIIc</u> <u>Wt%</u>	<u>IIId</u> <u>Wt%</u>	<u>IIIe</u> <u>Wt%</u>	<u>III f</u> <u>Wt%</u>
Luviset CA 66 ^(a)	0.4	--	--	--	--	--
Luviset CAP ^(b)	--	0.5	--	--	--	--
Sokalan EG 310 ^(c)	--	--	0.4	--	--	--
Ultraphold CA 8 ^(d)	--	--	--	1.0	--	--
Amerhold DR-25 ^(e)	--	--	--	--	0.75	--
Poligen A ^(f)	--	--	--	--	--	0.25
Silwet L-7600	0.15	--	--	--	--	--
Silwet L-7602	--	0.25	--	0.2	0.4	--
Silwet L-7604	--	--	0.2	--	--	0.15
Neodol 23-3	0.1	--	--	0.2	--	--
Diethylene glycol	0.3	--	0.1	0.5	0.2	0.15
Perfume	0.1	0.05	0.03	0.08	0.05	0.05
NaOH/HCl	to pH 9	to pH 9	to pH 8	to pH 8	to pH 7	to pH 7.2
Kathon CG	3 ppm	3 ppm	3 ppm	3 ppm	3 ppm	3 ppm
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

- (a) Vinyl acetate/crotonic acid copolymer.
- (b) Vinyl acetate/vinyl propionate/crotonic acid copolymer.
- (c) Polyvinylpyrrolidone/acrylic acid copolymer.

- (d) Ethyl acrylate/ acrylic acid/N-t-butyl acrylamide copolymer.
 (e) Ethyl acrylate/metacrylic acid/methyl methacrylate/acrylic acid copolymer.
 (f) Polyacrylate dispersion.

Examples III

The shape retention copolymer and the surfactant(s) are added with vigorous mixing into the water seat, which is pre-adjusted to about pH 12 using an aqueous NaOH (30%) solution. As the copolymer is slowly dissolved, NaOH solution is added to maintain the high pH. After about 1 hour of vigorous stirring, the composition is adjusted with HCl to the desired pH. Finally, diethylene glycol, perfume and Kathon preservative are added with agitation.

Examples Ingredients	Examples IV				
	<u>IVa</u> <u>Wt%</u>	<u>IVb</u> <u>Wt%</u>	<u>IVc</u> <u>Wt%</u>	<u>IVd</u> <u>Wt%</u>	<u>IVe</u> <u>Wt%</u>
Cartaretin F-23 ^(g)	1.0	--	--	--	--
Copolymer 937 ^(h)	--	0.3	--	--	--
Copolymer 958 ⁽ⁱ⁾	--	--	0.4	--	--
Diaformer Z-SM ^(j)	--	--	--	0.5	--
Vinex 2019 ^(k)	--	--	--	--	0.5
Lithium bromide	2.0	--	--	--	--
Lithium lactate	--	2.0	--	--	--
D5 volatile silicone	0.25	--	0.2	--	--
PDMS 10,000 cst	--	0.25	--	--	--
Silicone emulsion A	--	--	1.0	--	1.2
Silicone emulsion B	--	--	--	1.5	--
Silwet L-7602	0.3	--	--	--	0.1
Silwet L-7604	--	0.25	--	--	--
Silwet L-7622	--	--	0.5	--	--
Neodol 23-5	0.1	--	--	0.1	--
Diethylene glycol	--	--	0.2	--	--
Perfume	0.05	0.05	0.1	0.03	0.05
Kathon CG	3 ppm	3 ppm	3 ppm	3 ppm	3 ppm
Ethyl alcohol	--	10	--	--	--
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.

- (g) Adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer.
 (h) Polyvinylpyrrolidone/dimethylaminoethyl methacrylate copolymer.
 (i) Polyvinylpyrrolidone/dimethylaminoethyl methacrylate copolymer.
 (j) Methacryloyl ethyl betaine/methacrylates copolymer.
 (k) Polyvinyl alcohol copolymer resin.

Examples Ingredients	Examples V					
	<u>Va</u> <u>Wt%</u>	<u>Vb</u> <u>Wt%</u>	<u>Vc</u> <u>Wt%</u>	<u>Vd</u> <u>Wt%</u>	<u>Ve</u> <u>Wt%</u>	<u>Vf</u> <u>Wt%</u>

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Copolymer A ^(l)	0.4	--	--	1.0	--	--
Copolymer B ^(m)	--	0.5	--	--	--	--
Copolymer C ⁽ⁿ⁾	--	--	0.6	--	--	--
PVA ^(o)	--	--	--	--	1.0	0.5
Velustrol P-40 ^(p)	--	--	--	--	0.3	0.2
D5 volatile silicone	0.5	--	--	--	--	--
Silicone emulsion B	--	--	1.2	--	--	0.2
Silwet L-7600	0.4	--	--	--	0.25	--
Silwet L-7602	--	0.2	--	--	--	0.2
Neodol 23-5	0.2	--	0.1	0.1	--	--
Diethylene glycol	--	1.0	0.3	--	--	0.3
Glycerin	--	--	--	--	0.2	--
Perfume	0.05	0.05	0.08	0.1	0.03	0.05
NaOH/HCl	to pH 9	to pH 7	to pH 9	to pH 7	--	--
Kathon CG	3 ppm	3 ppm	3 ppm	3 ppm	3 ppm	3 ppm
Ethyl alcohol	--	--	--	--	5	--
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

(l) Acrylic acid/tert-butyl acrylate copolymer, with an approximate acrylic acid/tert-butyl acrylate weight ratio of about 25/75 and an average molecular weight of from about 70,000 to about 100,000.

(m) Acrylic acid/tert-butyl acrylate copolymer, with an approximate acrylic acid/tert-butyl acrylate weight ratio of about 35/65 and an average molecular weight of from about 60,000 to about 90,000.

(n) Acrylic acid/tert-butyl acrylate copolymer, with an approximate acrylic acid/tert-butyl acrylate weight ratio of about 20/80 and an average molecular weight of from about 80,000 to about 110,000.

(o) Polyvinyl alcohol, about 25,000 average molecular weight.

(p) Oxidized polyethylene emulsion.

Examples VI						
Examples ^(q) Ingredients	<u>VIa</u> Wt%	<u>VIb</u> Wt%	<u>VIc</u> Wt%	<u>VI d</u> Wt%	<u>VIe</u> Wt%	<u>VI f</u> Wt%
Copolymer D ^(r)	1.0	1.0	1.0	1.0	1.0	1.0
Neodol 91-2.5	0.1	--	--	--	--	--
Neodol 23-1	--	0.1	--	--	--	--
Neodol 23-3	--	--	0.1	--	--	--
Neodol 25-3	--	--	--	0.1	--	--
Neodol 23-5	--	--	--	--	0.1	--
Neodol 23-9	--	--	--	--	--	0.1
NaOH + HCl	to pH 9	to pH 9	to pH 9	to pH 9	to pH 9	to pH 9
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Examples Ingredients	<u>VIg</u> Wt%	<u>VIh</u> Wt%	<u>VIi</u> Wt%	<u>VIj</u> Wt%	<u>VIk</u> Wt%	<u>VI.l</u> Wt%
Copolymer D	1.0	1.0	1.0	1.0	1.0	1.0

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Neodol 23-12	0.1	--	--	--	--	--
Hetoxol TD-3	--	0.1	--	--	--	--
Hetoxol OL-5	--	--	0.1	--	--	--
Kessco PEG-8 Mono-oleate	--	--	--	0.1	--	--
Kessco Glycerol Mono-oleate	--	--	--	--	0.1	--
Arlacel 20	--	--	--	--	--	0.1
NaOH + HCl	to pH 9	to pH 9	to pH 9	to pH 9	to pH 9	to pH 9
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

(q) The alkyl ethoxylate surfactants used in these Examples, with approximate structure and HLB value, are as follows:

Name	Structure	HLB Value	Suppliers
Neodol 91-2.5	C9-C10 - 2.7EO	8.5	Shell Chemical Co.
Neodol 23-1	C12-C13 - 1.0EO	3.7	Shell Chemical Co.
Neodol 23-3	C12-C13 - 2.9EO	7.9	Shell Chemical Co.
Neodol 25-3	C12-C15 - 2.8EO	7.5	Shell Chemical Co.
Neodol 23-5	C12-C13 - 5.0EO	10.7	Shell Chemical Co.
Neodol 25-9	C12-C15 - 8.9EO	13.1	Shell Chemical Co.
Neodol 25-12	C12-C15 - 11.9EO	14.4	Shell Chemical Co.
Hetoxol TD-3	C13 - 3EO	7.9	Heterene Inc.
Hetoxol OL-5	Oleyl - 5EO	8.0	Heterene Inc.
Kessco PEG-8 Mono-oleate	Oleoyl - 8EO	11.0	Stepan Co.
Kessco Glycerol Mono-oleate	Glyceryl mono-oleate	3.8	Stepan Co.
Arlacel 20	Sorbitan mono-laurate	8.6	ICI Americas

(r) Acrylic acid/tert-butyl acrylate copolymer, with an approximate acrylic acid/tert-butyl acrylate weight ratio of about 23/77 and an average molecular weight of about 82,000.

Example VIa

Copolymer D and the nonionic surfactant are added with vigorous mixing into the water seat, which is pre-adjusted to about pH 12 using an aqueous NaOH (30%) solution. As the copolymer is slowly dissolved, NaOH solution is added to maintain the high pH. After about 45 minutes of vigorous stirring, the composition is adjusted to about pH 9 with HCl 1N, and mix further for about 15 minutes to obtain a water clear composition of Example VIa.

Examples VIb - VI l

Compositions of Examples VIb to VI l are prepared using the procedure of Example VIa, and using the appropriate surfactant. Only compositions VIc, VId and VIh

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are water clear, and composition VIe practically clear and clear up overnight, while the remaining compositions are cloudy at different degree.

The compositions of the above Examples are sprayed onto clothing using, e.g., the TS-800 sprayer from Calmar, and allowed to evaporate off of the clothing.

The compositions of the above Examples are sprayed onto clothing, using a blue inserted Guala[®] trigger sprayer, available from Berry Plastics Corp. and a cylindrical Euromist II[®] pump sprayer available from Seaquest Dispensing, respectively, and allowed to evaporate off of the clothing.

The compositions of the above Examples contained in rechargeable battery-operated Solo Spraystar sprayers are sprayed onto large surfaces of fabric, such as several pieces of clothing, and allowed to evaporate off of these surfaces. The level of coverage is uniform and the ease and convenience of application is superior to conventional manually operated trigger sprayers.

What is claimed is:

1. Aqueous clear composition comprising:
 - A. from about 0.05% to about 10% of (1) relatively water insoluble copolymer containing hydrophilic unsaturated organic monocarboxylic or polycarboxylic acid monomers, or salts thereof or mixtures thereof and hydrophobic monomers, and optionally other hydrophilic monomers and/or (2) silicone-containing copolymers;
 - B. from 0.01% to about 5% of alkyl polyethoxylate surfactant having a C₈-C₁₆ alkyl group and containing from about 2 to about 6 ethyleneoxy groups;
 - C. optionally, from about 0.01% to about 5% of silicone surfactant;
 - D. optionally, containing at least one of lithium salt, silicone, perfume, odor control agent, antimicrobial active, antibacterial preservative, aminocarboxylate chelator, low molecular weight polyol, static control agent, insect repelling agent and/or moth repelling agent; and
 - E. the balance essentially water.
2. The composition of Claim 1 wherein in (1) said hydrophilic unsaturated organic mono-carboxylic or polycarboxylic acid monomers are selected either: (a) from the group consisting of: low molecular weight C₁-C₆ unsaturated organic monocarboxylic and polycarboxylic acids, and mixtures thereof; and the hydrophobic monomers are selected from the group consisting of esters of said acids with C₁-C₁₂ alcohols; esters of low molecular weight unsaturated alcohols with low molecular weight carboxylic acids; ethers of said low molecular weight unsaturated alcohols; and mixtures thereof; (b) are selected from the group consisting of: acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and mixtures thereof; and the hydrophobic monomers are selected from the group consisting of esters of said acids with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, and mixtures thereof; (c) are selected from the group consisting of: acrylic acid, methacrylic acid, and mixtures thereof; and the hydrophobic monomers are selected from

the group consisting of esters of said acids with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, t-butanol, and mixtures thereof; or (d) said copolymer contains acrylic acid and tert-butyl acrylate monomers in a weight ratio of from about 40:60 to about 20:80 and an average molecular weight of from about 30,000 to about 300,000, or, preferably, in a weight ratio of from about 25:75, to about 35:65 and an average molecular weight of from about 60,000 to about 100,000.

3. The composition of any of Claims 1-2 wherein said polymer (2) comprises silicone-containing graft and block copolymers having the following properties:

- (1) the silicone portion is covalently attached to the non-silicone portion;
- (2) the molecular weight of the silicone portion is from about 1,000 to about 50,000; and

the non-silicone portion containing hydrophilic unsaturated organic monocarboxylic or polycarboxylic acid monomers, or salts thereof or mixtures thereof, and optionally hydrophobic monomers, and other hydrophilic monomers, said non-silicone portion must render the entire copolymer soluble or dispersible in the wrinkle control composition vehicle and permit the copolymer to deposit on/adhere to surfaces treated therewith, and preferably wherein said polymer has an average molecular weight of from about 10,000 to about 1,000,000, preferably from about 30,000 to about 300,000, and comprises from about 5% to about 50%, preferably from about 10% to about 25%, of silicone containing monomers, and wherein, preferably, said polymer comprises silicone-containing monomers exemplified by the general formula:



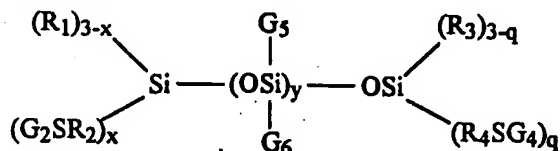
wherein X is a polymerizable group, such as a vinyl group, which is part of the backbone of the polymer; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl, aryl, alkaryl, alkoxy, or alkylamino group; Z is a monovalent polymeric siloxane moiety having an average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to about 3.

4. The composition of any of Claims 1-3 wherein said silicone containing polymer comprises one or more silicone-containing block copolymers having one of the formulas A-B, A-B-A, and $-(A-B)_n-$ wherein n is an integer of 2 or greater; in which A-B

represents a diblock structure, A-B-A represents a triblock structure, and $-(A-B)_n-$ represents a multiblock structure and in which said block copolymers can comprise mixtures of diblocks, triblocks, and higher multiblock combinations as well as small amounts of homopolymers, the group B, being represented by the following polymeric structure



wherein each R is independently selected from the group consisting of hydrogen, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, C₂-C₆ alkylamino, styryl, phenyl, C₁-C₆ alkyl or alkoxy-substituted phenyl; and m is an integer of about 10 or greater; the non-silicone block, A, comprises monomers selected from the group consisting of low molecular weight C₁-C₆ unsaturated organic mono- and polycarboxylic acids; esters of said acids with C₁-C₁₂ alcohols; amides and imides of said acids; low molecular weight unsaturated alcohols; esters of low molecular weight unsaturated alcohols with low molecular weight carboxylic; ethers of said low molecular weight unsaturated alcohols; polar vinyl heterocyclics; unsaturated amines and amides; vinyl sulfonate; salts of said acids and said amines; C₁-C₄ alkyl quaternized derivatives of said amines; low molecular weight unsaturated hydrocarbons and derivatives; and mixtures thereof, the block copolymers containing at least one non-silicone block, and up to about 50%, by weight of one or more polydimethyl siloxane blocks and/or wherein said polymer comprises sulfur-linked silicone containing copolymers, including block copolymers represented by the following general formula:



wherein

each G₅ and G₆ is independently selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and —ZSA, wherein A represents a vinyl polymeric segment consisting essentially of polymerized free radically polymerizable monomer, and Z is a divalent linking group;

each G₂ comprises A;

each G₄ comprises A;

each R₁ is a monovalent moiety selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and hydroxyl;

each R₂ is a divalent linking group;

each R_3 represents monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and hydroxyl;

each R_4 is a divalent linking group selected from the group consisting of C_{1-3} alkylene and C_7-C_{10} alkarylene;

x is an integer of 0-3;

y is an integer of 5 or greater; and

q is an integer of 0-3;

wherein at least one of the following is true:

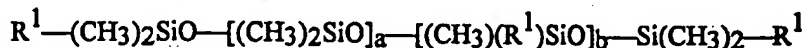
q is an integer of at least 1;

x is an integer of at least 1;

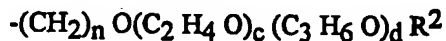
G_5 comprises at least one —ZSA moiety; or

G_6 comprises at least one —ZSA moiety.

5. The composition of any of Claims 1-4 wherein said alkyl polyethoxylate surfactant contains from about 2 to about 4 ethyleneoxy groups and preferably either (a) has a C_8-C_{15} alkyl group and contains from about 2.25 to about 3.5 ethyleneoxy groups, (b) has a C_8-C_{16} alkyl group and contains from about 2 to about 4 ethyleneoxy groups, or (c) has a C_8-C_{15} alkyl group and contains from about 2.25 to about 3.5 ethyleneoxy groups and, wherein, when present, said silicone surfactant is, optionally, polyalkyleneoxide polysiloxane having the general formula:



wherein $a + b$ are from about 1 to about 50, and each R^1 is the same or different and is selected from the group consisting of methyl and a poly(ethyleneoxide/propyleneoxide) copolymer group having the general formula:



with at least one R^1 being a poly(ethyleneoxide/propyleneoxide) copolymer group, and wherein n is 3 or 4; total c (for all polyalkyleneoxy side groups) has a value of from 1 to about 100; d is from 0 to about 14; $c+d$ has a value of from about 5 to about 150; and each R^2 is the same or different and is selected from the group consisting of hydrogen, an alkyl having 1 to 4 carbon atoms, and an acetyl group.

6. The composition of any of Claims 1-5 containing either (a) from about 0.1% to about 5% by weight of the composition of said copolymer and from about 0.05% to about 3% by weight of the composition of said surfactant; (b) from about 0.2% to about 3% by weight of the composition of said copolymer and from about 0.1% to about 2% by weight of the composition of said surfactant; or (c) from about 0.3% to about 1.5% by weight of the composition of said copolymer and from about 0.2% to about 1% by weight of the composition of said surfactant.

7. The process of solubilizing a copolymer of any of Claims 1-6 by adding the surfactant of any of Claims 1-6 to an aqueous dispersion containing said copolymer.

8. An article of manufacture comprising the composition of any of Claims 1-6 in a spray dispenser optionally either: (a) comprising a trigger spray device; (b) comprising a pressurized aerosol spray dispenser; or (c) comprising a non-manually operated spray dispenser optionally selected from the group consisting of: powered sprayer; air aspirated sprayer; liquid aspirated sprayer; electrostatic sprayer; and nebulizer sprayer.

9. The article of manufacture of Claim 8 in association with instructions to use the composition at an effective level, optionally in combination with stretching and/or smoothing of fabric, to provide effective wrinkle removal.

10. A method of controlling wrinkles on fabric comprising spraying an effective amount of the composition of any of any of Claims 1-6 onto said fabric using a spray dispenser, optionally in an article of manufacture according to Claim 8 wherein, preferably, the droplets of the spray that are formed by the spray dispenser have a weight average diameter of from about 5 μm to about 250 μm , and optionally in combination with stretching and/or smoothing of fabric.

INTERNATIONAL SEARCH REPORT

Int. onal Application No

PCT/US 99/08948

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D06M15/263 D06M15/643 D06M15/53 D06M13/148 D06M11/13
D06M23/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 532 023 A (VOGEL ALICE M ET AL) 2 July 1996 (1996-07-02) cited in the application column 1, line 55 - column 17, line 38 ---	1,2,4-10
X,P	WO 98 56890 A (PROCTER & GAMBLE) 17 December 1998 (1998-12-17) page 3, line 10 - page 6, line 10 page 14, line 1 - page 17, line 29 page 36, line 33 - page 53, line 10 page 53, line 12 - page 62, line 15; claims ---	1-10
X	WO 96 15310 A (PROCTER & GAMBLE) 23 May 1996 (1996-05-23) page 2, line 20 - page 20, line 24; claims; examples --- -/-	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

18 August 1999

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INTERNATIONAL SEARCH REPORT

Inter national Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 3 436 772 A (STEBBINS DAVID T) 8 April 1969 (1969-04-08) cited in the application the whole document</p> <p>-----</p>	8

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